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Printability and environmental testing using silver-based conductive flexographic ink printed on a polyamide substrate

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Printability and Environmental Testing using Silver-based Conductive Flexographic Ink Printed on a Polyamide Substrate

by Kathryn O. Cole

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Printability and Environmental Testing using Silver-based Conductive Flexographic Ink Printed on a Polyamide Substrate

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In loving memory of PFC David Michael Cole, Sr.

Whose fatherly guidance and encouragement

I carry with me everyday of my life

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Abstract

The effect of simulated environmental exposure conditions (high heat, freezing temperature, rain, and vacuum pressure) on the performance of a silver-based conductive flexo ink printed on a polyamide (nylon 6,6) substrate was examined. Conductivity, density, color, adhesion, abrasion resistance and creasing were evaluated.

The tested environmental variables did not have an effect on the performance quality of silver conductive flexographic ink when printed on a polyamide substrate for the 85 – 100% solid ink density levels. Rain and temperature had the greatest impact on print performance in the 70–80% tint range. Exposure to these elements affected adhesion properties of the ink to the substrate, which lead to a negative effect on the conductivity and abrasion performance.

This study indicated an antenna printed at common ink density levels using a silver-based flexographic printing ink on a polymeric film is a possible solution for the implementation of printed RFID components. This is a manufacturing option that can bring the packaging industry from a "slap and stick" RFID labeling method to an actual inline production method that can be applicable to both primary and secondary package tagging needs. Lastly, the study utilizes common ink testing procedures that will be useful in the development of standards for the production of printed RFID components in packaging applications.

Chapter 1

Introduction

Introduction

An area of growth opportunity for the print industry driven by demand from large retail and manufacturing customers is printed electronics (IDTechEx, 2006). One of the current main products of the printed electronics industry is printed radio frequency identification (RFID) components. RFID technology has been in use for several years but advances in printing materials and methods have finally permitted the possibility of a fully printed RFID tag. This advancement has lead to a potential market share in the billions of dollars. Harrop (2006) believes that by the year 2016, the RFID market will grow to a value of $26.23 billion. Printers can capitalize on this market by creating a low cost but highly effective fully printed RFID tag for use in product packaging. To achieve this, significant research in the area of materials and end-use performance testing is needed to develop a set of standards for the industry to follow.

The research conveyed in this study provides valuable information for materials testing of a commonly used silver-based flexographic ink for use in typical product packaging applications. The researcher exposed sample prints to varying simulated environmental conditions a package might endure. A set of ink-testing procedures was conducted to determine the effect, if any, on the performance of the ink by comparison to a controlled environmental condition.

Statement of the Problem

The effect of simulated environmental exposure conditions (vacuum, rain, freezing temperature, and high heat) on the performance of a silver-based conductive flexo ink printed on a polyamide (nylon) substrate was studied. Using a set of standard ink tests—conductivity, density and color, abrasion, creasing, and ink adhesion—significant results were explained with a comparative analysis to a controlled environment.

Reason for Interest

The researcher became interested in a scientific approach to the study of printing materials through course work done in the Materials and Processes class at the Rochester Institute of Technology. In pursuance of a Master's Degree in Print Media, the researcher chose to study in a new, but growing market of materials science of the printing industry called RFID technology.

Upon conducting a study of the literature regarding RFID technology and its connection with the printing industry, the graduate student discovered an area where research on materials used in the production of printed electronics, specifically RFID ink, was needed for the industry to progress. It was found that a potential major user of RFID ink is the packaging industry. This led the researcher to conduct her thesis in the area of simulating RFID ink printing, usage, and testing in the packaging environment.

Chapter 2

Theoretical Basis

Ink Principles

Determination of Ink Testing

End uses of various packaging applications were considered in the selection of ink testing procedures for this experiment. Storage and shipping environments were the main consideration for the choice of simulated environments however, primary packaging applications were also considered. Ink tests of conductivity, density, color, adhesion, abrasion resistance and creasing were the chosen ink testing methods. This was based on standard end use ink testing procedures set forth by the examination of a study published by Jonathan Collins, of Precisia formerly a subdivision of Flint Ink in RFID Journal (Collins, 2003).

The study by Collins indicates that one of the critical factors to the successful printing of conductive antennas is thickness of the ink film or level of ink density. At the time, there was not a set standard in place with regards to minimum required density level to achieve an acceptable level of conductivity of an ink patch for the use of antenna production (Collins, 2003). Therefore, it was determined that conducting the chosen tests over several ink density levels would give valuable data with regards to this matter. This is why a proofing plate with varying tint percentages from 100 – 60% density levels was chosen.

The key ink quality factors that Collins suggests, should be considered as standard testing procedures for printed antenna production are color, optical density, rub resistance, the effect of creasing and the adhesive qualities of the ink. He also goes on to say that these qualities should be tested with mind to electrical resistivity, crease resistance, temperature, and humidity effects on the performance of the inks (Collins, 2003). These were key factors that drove the setup of the thesis testing procedures and selection of simulated environmental conditions.

Substrate Principles

Nylon Substrates

Nylon along with most linear polymers is a glass at low temperatures. As the temperature is increased, the polymer changes from a glass to a rubber at a certain point. This is known as the glass transition temperature or T_g. Nylon being a crystalline polymer, remains thermoplastic or flexible above the T_g level until it reaches the crystalline melting temperature (T_m), in which it begins to melt and transform into a liquid state. For nylon 6,6 these two states occur at T_g= 113^o F (45^o C) and T_m= 512.6^o F (267^o C) (Allcock, Lampe, Mark, 2003).

Nylon 6,6 film is a viscoelastic material. This means that it has the characteristics of both solid and liquid states (Allcock, Lampe, Mark, 2003). Nylon 6,6 film posses the characteristics of the glassy or brittle state at room temperature (70^o F, 21.1^o C), the state in which the print samples for this study were created and also at 45^o F (7.2^o C), the temperature at which the rain condition was simulated. It also exhibits characteristics of the rubbery state at the temperature of 140^{o} F (60^{o} C), which is the temperature that the heat condition was simulated.

Print Production Principles

Color Space

The form of color space system that was used in this study is the CIE LAB (L*a*b*) system. CIE stands for Commission Internationale de l'Eclairage or International Commission on Illumination. This system uses a measuring instrument (in the case of this study, X-Rite DTP 22 Model handheld spectrophotometer) to sample a color and produce a numerical representation of that color. The use of CIE LAB color system allows the quantification of the color to be device independent through the incorporation of special calculations that allows the mimicking of human vision (Sharma, 2004). In this experiment a determination of 2^{o} observer angle with a D50 Illuminant at a 45^{o} angle was measured to mimic the human eye's vision at a close up distance. The CIELAB system identifies a specific color by coordinating 3 different measurements (L*a*b*) to a position in a 3D color space. The L* stands for lightness, a* represents the position of the color on a red-green axis, and b* represents the position of the color on a yellow-blue axis (Sharma, 2004).

Rheology

Rheology is the study of deformation and flow. Viscosity is the property of fluids that indicates resistance to flow. When a force is applied to a volume of material then a displacement (deformation) occurs. In relation to printing inks, the concentration of dissolved or dispersed pigments in the ink can sometimes cause more resistance to flow. An increase in viscosity is known as shear thickening (Chaplin, 2006). Shear thickening is a common occurrence with conductive inks because the metallic particles that created conductivity in the ink are often larger than traditional pigments. Therefore, there are often shear thickening problems with conductive inks and the press setting must be adjusted accordingly.

Surface Tension

Surface tension, in terms of the printing industry is defined as the property of a substrate that relates to how receptive the surface of the substrate is to accepting printing inks (Flexography Principles and Practices, 1999.) In ink, the molecules at the surface are held together more strongly to those directly associated with the surface. This occurrence forms a surface "film" which has a force greater than the force acting upon the molecules below the surface of the liquid. Surface tension is typically measured in dynes/cm, the force in dynes required to break a film of length one centimeter. Water at 68^{o} F (20° C) has a surface tension of 72.8 dynes/cm. The surface tension of the ink and the substrate were measured to ensure that the ink had sufficient wetting (ability of the ink to adhere to the surface of the substrate when printing at a certain speed) capabilities to create an acceptable print sample. In order for this to be true, the ink had to posses a lower surface tension than that of the substrate. For proper adhesion to occur, the dyne level of the ink should be ten dynes/cm lower than the dyne level of the substrate (Vainstein, 2005). If the ink did not have a lower measurement, the ink would not “stick” to the surface of the substrate. Subsequently, the substrate would need to be corona treated to raise the surface tension thus allowing the ink to transfer to the substrate (Podhajny, 2004). The surface tension of the nylon 6,6 film used in this experiment measured 50 dynes/cm and the ink used measured 40 dynes/cm. Therefore, it was determined that the ink did posses sufficient wetting capabilities and the substrate did not need corona treatment.

Packaging Principles

Primary Packaging

Primary packaging is defined as packaging that immediately envelopes a product. It provides most of the strength and the moisture, vapor or grease barrier needed to safeguard a product's purity, potency and integrity from the time it leaves the assembly line until it's used by the consumer. Examples of primary packaging include blister packs, clamshells and trays. (assemblymag.com, n.d.)

Secondary Packaging

Secondary packaging is defined as material used primarily to give additional physical protection to the outside of a proximity package. Examples of secondary packaging include cartons, containers, pallets, cardboard boxes, padded bags, and polythene wrap (ESD Guide, 2005).

Role of Nylon in Packaging

Because nylon has many desirable properties such as good thermal, chemical and oil/grease resistance and also good formation properties it is a material that works well as solution for various primary and secondary packaging needs (British Plastics Federation, 2003). Many packaging uses of nylon film are for food and pharmaceutical “clean packaging” needs (Nappi, 2004). It is also used in blister pack applications where it is vacuum or thermo formed (Selke, Cutler, Hernandez, 2004).

Other Principles

Definition of Ohms/square

Ohms/square is a quantitative method to measure surface resistivity of a material. Gene Chase of ETS, Inc. (n.d.) defines surface resistivity as the resistance between two opposite sides of a square and is independent of the size of the square or its dimensional units. This term is used to describe any dimension of a resistive material and is especially useful in describing thin and thick film antennas because of their variance in size and amount of conductive material used in the manufacture of these devices. The basic principle of using ohms/square when referring to surface resistivity is to divide the surface of the conductive plane (in the scope of this experiment, the surface of the antenna) into any number of squares (in this case centimeters) and measure resistivity in ohms over the distance of the predetermined square. This will indicate the level of resistance to conductivity of the material being measured. The lower the resistance measurement in ohms/square, the more conductive the material is (Chase, n.d.).

Determination of Acceptable Resistance Limitation

In the production of RFID antennas, there is not a set standard level of maximum permitted resistance of a conductive material. This is because the conductivity level that is needed to create a functional antenna is dependent upon the read range needed for the tag and also the level of data capabilities of the tag. Antennas that require a longer read range require a higher conductivity level and thus demand a lower acceptance limitation level for surface resistivity. For the scope of this project it was determined that an acceptable limit of resistivity is 25 ohms/square or less. This was derived from the examination of US patent number 6,870,516 (Aisenbrey, 2006). In this patent, Aisenbrey establishes that a desirable usable range of resistivity for the production of RFID antennas using a conductive loaded resin-based material is between 5 and 25 ohms/square. Therefore, for the purpose of this project it was determined that the acceptable limit of resistivity of the print samples was 25 ohms/square or less.

Notations

Table 1: List of units used in experiment

L*	Represents lightness in color space.
a*	Represents the position of color on the red-green axis.
b*	Represents the position of color on the yellow-blue axis.
Dynes/cm	The force required to break the surface of a film the length of one centimeter. Used to measure surface tension of a substrate or ink.
Ohms/square	The measure of the inherent resistance to electrical current flow across the surface of a material. Used to measure resistance to conductivity over a square surface of conductive material.

Chapter 3

Literature Review

Introduction

Radio Frequency Identification (RFID) technology is currently in the early stages of adoption in various manufacturing and retail markets. One of the major factors that will contribute to the item-level adoption of RFID tagging is the successful production of a fully printed RFID tag. There are many issues surrounding the adoption of printing methods as a viable solution for the industry. However, with continued research and development, these issues are likely to be solved, and market potentials for printed RFID tags and their incorporation into the packaging industry are great.

RFID Technology Basics

RFID systems transmit signals through electromagnetic or electrostatic coupling in the radio frequency (RF) portion of the electromagnetic spectrum (Technovelgy, n.d.). RFID is used to identify people or objects, and it functions somewhat similarly to barcoding. The RFID can transmit a single piece of data, such as a serial number, or it can send very detailed data about the object or person that can include where it came from, where it is going, and how it is being transported. The data is transmitted from a chip encoded with information through an attached antenna. The antenna sends the signal to a reader device that is usually connected to a data collection/storage unit such as a computer (RFID Journal, 2006).

An RFID tag houses two of the main components, the antenna and chip. Traditionally, these components have been produced using a labor-intensive process with expensive materials. The antenna was made from a thin copper film created using a stamping process. The chip was made from silicone and metal circuit boards that had to be manufactured in a clean-room environment. However, in current RFID tag production, most of the antennas are now printed using conductive inks, and although not yet in the production stage, chip production is also moving toward a printed manufacturing process.

There are three types of tags in RFID technology: active, passive, and semi-passive. An active tag broadcasts the signal using its own power source, a battery that is contained within the tag. It has a read-range of about 100 yards, provided that there is little interference with the tag's transmission in its immediate surroundings. A passive tag does not have a battery. Passive tags function through harnessing power supplied to the tag from the electromagnetic waves sent from the reader. The tag then uses the antenna to send the signal back to the reader. This is known as backscatter reflection. The signal that is sent from a passive tag has a shorter read-range and uses amplitude modulation to send binary data to the reader. A semi-passive tag has the same properties of the passive tag. It is lightweight and small in size and has a limited memory, but it also has a battery that extends the read-range further than that of the passive tag (Kleist, Chapman, Sakai, & Jarvis, 2004). In addition to different types of tags, there are also different brands of tags, each with different characteristics. The Table 1 describes the different brands of RFID tags and their properties.

Table 2: Brand description of RFID tags (Kleist et al., 2004)

Brand	Frequency	Read Range	Typical Application
Low Frequency (LF)	100-500 kHz	Up to 20 inches (50.8 cm)	Access control, animal identification, vehicle anti-theft system
High Frequency (HF)	13.56 kHz	Up to 3 feet (1 meter)	Access control, smart cards, item level tagging, libraries, and electronic article surveillance
Ultra-high Frequency (UF)	866 – 956 MHz	FCC allows over 20 feet (6 meters) at 915 MHz. Range at 866 MHz is about 10% less than at 915 MHz.	Supply chain use, baggage handling and toll collection. Wal-Mart acceptance.
Microwave	2.4 GHz	3 to 10 feet (1 to 3 meters)	Item tracking, toll collection

History of RFID

The beginning of RFID technology is often traced back to its use in the tracking of fighter airplanes in World War II. In 1939, the British developed a system called Identify Friend or Foe (IFF) in which they placed a transmitter on British planes that sent radar signals to the base identifying the aircraft as friendly. Throughout the 1950s and 1960s, most of the development of RFID technology came from research done by universities and scientists. Several papers were published on the application of RF energy for use in remotely identifying objects (RFID Journal, n.d.).

In 1973, the first major event in RFID history occurred when Mario Cardullo received the first patent in the United States for an active RFID tag with rewritable memory. Later that same year, Charles Walton received a patent for a passive transponder. The transponder was used to create a device that would allow a door to open without the use of a key (RFID Journal, n.d.).

The U.S. government also began testing the use of RFID systems in the 1970s. The Los Alamos Laboratory was commissioned by the Energy Department to develop an RFID system for tracking nuclear materials. This system involved placing transponders with information about the materials on the truck. The transponders were linked to the driver's identification, allowing access to the destination facilities. The Agriculture Department also commissioned the Los Alamos Laboratory to create a way of tracking cattle for medicinal purposes using RFID technology. They were able to ensure that the cattle were not given the incorrect dosage of hormones and medicines. This method used a glass capsule that was injected under the cow's skin. The capsule contained a 125 kHz transponder activated by the signal sent out by a reader. After creating many successful RFID systems for Los Alamos, some of the scientists left the laboratory and began commercializing similar systems in the mid-1980s for road and bridge toll payment systems. These RFID systems are still in use for these same purposes around the world (RFID Journal, n.d.).

Over time, 125kHz systems became inefficient for commercial applications. A high-frequency (13.56 MHz) radio spectrum system was developed with greater read-range and faster transfers. Common applications for this technology are found in contactless smartcards for payment options and as anti-theft devices in some automobiles. Also, this frequency is widely used in Europe for tracking reusable containers in manufacturing operations. The ultra-high frequency RFID system was developed in the early 1990s by IBM. This technology allowed for much longer read-ranges (up to 20 feet) and much faster data exchange (RFID Journal, n.d.). In 1999, the Uniform Code Council (UCC), EAN International, Proctor & Gamble, and Gillette funded the creation of the Auto-ID Center at the Massachusetts Institute of Technology. Between 1999 and 2003, Auto-ID Center developed protocol standards (Class 1 and Class 0) and the Electronic Product Code (EPC) numbering system and licensed it to the UCC, which created an organization called EPCglobal to commercialize EPC technology (RFID Journal, n.d.).

The years 2000–2006 have been a time of expansion for RFID systems amongst retailers and manufacturers alike, most notably, Wal-Mart, the U.S. Department of Defense, Albertsons, Target, Tesco, and others. EPCglobal has recently updated standardization with the presentation of the Gen2 standard in December of 2004 (RFID Journal, n.d.). The most recent main activity is focused around finding an economically feasible method for creation and application of an entire RFID chip and antenna. The industry has focused its research in developing various printing methods using conductive inks to create a fully printed chip. Evidence of this direction has recently been published in market forecast reports such as those created by IDTechEx and RFID Journal.

Overview of Conductive Inks

Conductive inks are primarily composed of metallic flakes, usually silver or copper, or carbon flakes that are suspended in a retaining matrix. A retaining matrix is traditionally composed of a ceramic material such as glass frit; however, since conductive ink formulations have progressed, the retaining matrix now tends to be typically made of polymers, which are known as Polymer Thick Films (PTFs). The retaining matrix is not inherently conductive although it may be weakly conductive.

Once the ink is printed, the retaining matrix must be reduced to allow the ink to be conductive. The ink becomes conductive when the retaining matrix is removed and the metallic or carbon particles come in contact with each other. This process of reducing the retaining matrix is known as curing. In conductive inks, this can be performed through a number of methods (e.g., UV, heat-curing). Typically, PTF ink formulations have a lower curing temperature of 150^{o} C, which allows for more options for substrate selection and is particularly useful with flexible polymer films (IDTechEx, 2004). Flexographic conductive inks, since they are water-based, typically cure through evaporation of the solvent into the air.

The difference between carbon-based and metallic-based conductive inks is that carbon inks are generally two magnitudes less conductive than metallic inks and therefore provide for a weaker signal and less read-range when used in RFID applications. However, carbon-based inks are more economical to produce and are less environmentally hazardous than metallic-based inks (IDTechEx, 2004).

Carbon inks are typically used in EMI/RF shielding applications, such as their use in speakers and monitor screens because of their weak conductivity (IDTechEx, 2004). Currently, much research is being done to improve and develop better carbon and organic-based inks because they are much more environmentally compatible and would require less regulation and containment in production of printed electronic products.

Metallic inks are currently used in a wide array of printed electronic applications such as membrane switches and circuits, RFID tag antennas, smart package and tamper-evidence packaging, and printed battery testers (IDTechEx, 2004). Applications of conductive metallic inks that are currently in the research and standards development stage that will enter production in are printed RFID chips, flexible photovoltaic arrays, and printed batteries, among others (Carli, 2006).

Conductive inks, both metallic and organic, are typically formulated to provide properties to suit a specific substrate and printing process (IDTechEX, 2004). Currently, conductive inks have been developed for use in all forms of print methods (inkjet, screen, flexography, gravure, offset litho) with the exception of toner-based electrostatic printing. Most producers (DuPont, XInk) provide several different lines of conductive inks for these different printing applications. There are other ink companies that are working on developing a single ink for use with multiple substrates and printing applications as well (IDTechEx, 2004).

Printed RFID and Packaging

Several factors are driving the use of RFID technology in the packaging industry, but the main reason for its use is to replace Universal Product Code (UPC) and barcoding technology (Harrop, 2002). RFID technology has been successfully adopted for use on the palette and crate level for the management of supply chain for various retailers and manufacturers; the most predominate of these are Wal-mart and the U.S. Department of Defense.

The use of an RFID tagging system is not currently feasible for item-level packaging because of the cost of production and the complicated methods of manufacturing the tags. Making RFID tagging feasible can be accomplished through creating the components of RFID tags by directly printing the conductive inks on the packaging substrate. Printers have printed an RFID tag directly onto a substrate, but this has only been done in research applications. At this point, a system for use in manufacturing and packaging production has not yet been reached. Product manufacturers indicate that they will invest in printed RFID tag systems for their packaging needs but not until costs can be reduced. The markets for item-level packaging applications currently using some form of RFID tagging include libraries, media merchandisers (DVDs, CDs, books, etc.), and pharmaceuticals (Casatelli, 2006). Other industries will include RFID in their packaging solutions once other challenges have been eliminated. The main examples of these challenges have been identified as a lack of standardization and performance problems relating to the environment and interference (Harrop, 2002).

Conclusion

As materials and methods improve for producing RFID tags directly onto packaging, more market adoption will be seen. The major issues that need to be resolved are production efficiency and costs, but customers identify performance and standardization as hot topics to be addressed as well. Many industries currently using RFID technology, as well as many of the potential markets, indicate that if these conditions improve, they will invest in printed RFID to serve the needs of their clients.

Chapter 4

Research Statement

The effect of simulated environmental exposure conditions (vacuum, rain, freezing temperature, and high heat) on the performance of a silver-based flexographic RFID ink printed on a polyamide (nylon) substrate was studied. Using a set of standard ink tests—conductivity, density and color, abrasion, creasing, and ink adhesion— significant results were explained by a comparative analysis against a controlled environment.

Research Questions

Can conductive ink withstand conditions a printed RFID tag would be exposed to in the primary or secondary level packaging supply chain?

Does exposure to environmental elements have an effect on the performance of a silver-based conductive flexographic ink?

What is the optimum ink density level for printing RFID components with a silver-based conductive ink?

Chapter 5

Methodology

Materials

Substrate

The substrate that was used in this experiment is a polyamide (PA) commonly known as nylon. Nylon is classified as a condensation copolymer. It is a linear thermoplastic polyamide that contains the amide group as a recurring part of its chemical chain. Nylon can be made through the condensation of amino acids that contain both amine and acid functional groups in a single molecule, or they can result from the condensation of diamines and dibasic acids. In this experiment, DuPont DARTEK® cast nylon 6,6 film was used to create the print samples. This material is created through the condensation polymerization of hexamethylene diamine and adipic acid. The formula for this reaction is shown in Equation 1.

$$\underset{\text{(Hexamethylene diamine)}}{H_2N\text{-}(CH_2)_6\text{-}NH_s} \quad + \quad \underset{\text{(Adipic acid)}}{HOOC\text{-}(CH_2)_4\text{-}COOH} \Leftrightarrow \tag{1}$$

$$\underset{\text{(Nylon 6,6)}}{\begin{array}{c} H \\ | \\ H \end{array} \!\!—[N — (CH_2)_6 — \begin{array}{c} H \\ | \\ N \end{array} — \begin{array}{c} O \\ || \\ C \end{array} — (CH_2)_4 — \begin{array}{c} O \\ || \\ C \end{array}]_n — OH}$$

The numerical suffix specifies the numbers of carbons donated by the monomers. The first number represents the number donated by the diamine and the second represents the number donated by the diacid. In this case, both the diamine and the diacid donate six carbon atoms (Selke, Culter, & Hernandez, 2004).

This film was chosen because it is a common film used in the production of bags, tubing, sheets, and sleeves for packaging purposes. It is usually used in film form as a single component or combined into multilayer structures with other polymers in a film. Some of the properties of this film are that it retains its properties over a broad temperature range as it remains flexible as low as -100°F (-73°C) and it will withstand temperatures up to 450°F (232°C). Dependent on environmental conditions, it has good barrier resistance to gases, odors, oils, and greases but is hydrophilic, so it can soak up moisture. It has an O_2 permeability of 3-5 cc/100in2/day. It has a thickness of 0.60 mil to 5.0 mil and will be cut down to a size of five inches by nine inches (DuPont, 2006).

To ensure material specifications prior to the samples' print run for the testing process, the researcher conducted a test using a Fourier Transform Infrared (FTIR) spectrometer. Infrared (IR) spectroscopy is a chemical analytical technique that detects the vibration characteristics of chemical functional groups in a sample (in this case, DuPont DARTEK®). When infrared light interacts with the sample's matter, the chemical bonds present in the sample will contract and stretch. When this happens, the certain chemical functional groups will absorb the IR radiation in a specific wavenumber. These specific wavenumbers are identifiable in a graph of the spectrum that can be created with the aid of a computer program that interprets the IR data. The chemical functional groups are seen in the peaks and valleys of the spectrum graph (NUANCE, 2006). The FTIR spectrum of the substrate sample confirmed the material is nylon 6,6 (Figure 1).

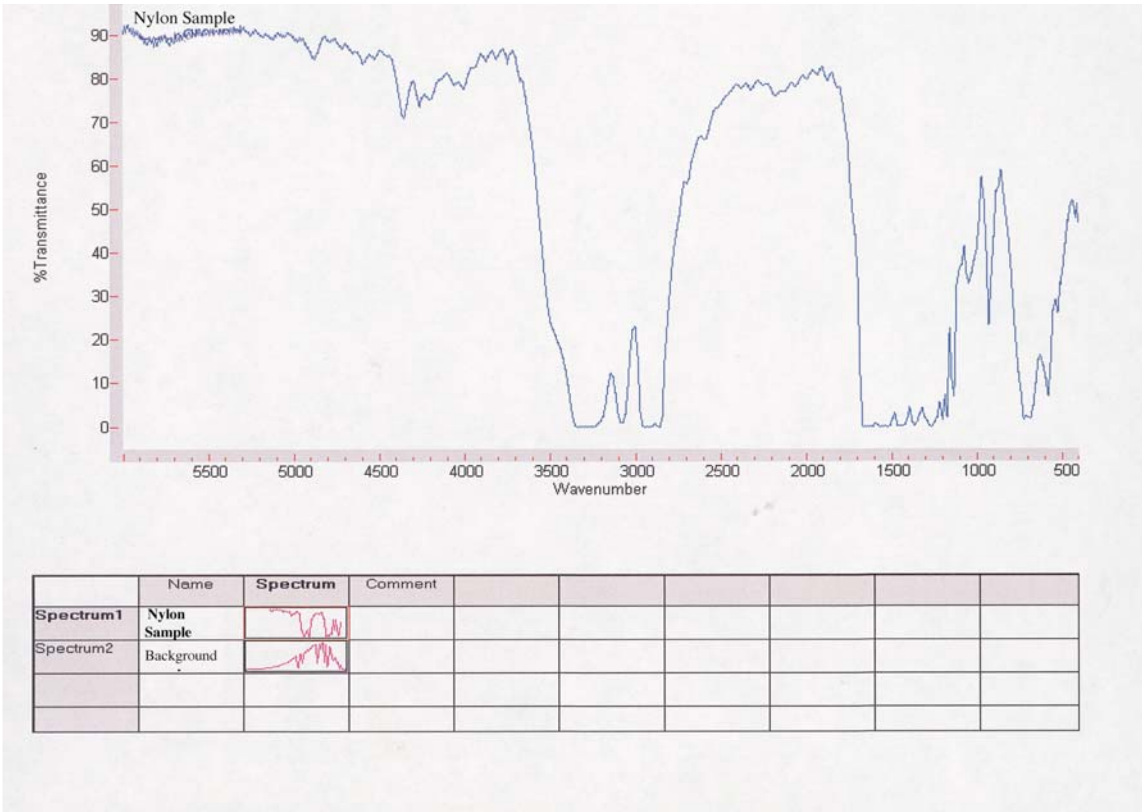

Figure 1: FTIR spectrum of DuPont DARTEK® substrate sample

The final step in preparing the substrate for printing the samples for the experiment was to determine the surface tension of the substrate and compare it with the surface tension of the ink. This was done to ensure there would be effective adhesion of the ink to the substrate and to determine that corona treatment of the film was not needed. Surface tension is the work per unit area required to reshape a liquid. It is measured in dynes/cm. For the ink to wet the surface of a substrate, the surface tension of the ink must be lower than the substrate surface tension (Chemical Fabrics & Film Association, n.d.).

To ensure that the substrate that was going to be used in this experiment possessed a surface tension higher than the ink, a dyne test was performed. This was done using a set of dyne solutions that ranged from 30 to 60 dynes/cm. The test was performed by dipping a sponge applicator wand into the solution and dragging it across the surface of the substrate starting with the 30 dyne/cm solution. Determining the dyne level of the substrate's surface in this type of test is done once the solution has been spread onto the surface of the substrate. The researcher conducting the test counts two seconds, and if the solution has beaded up on the surface of the substrate, the dyne solution is a lower level than that of the substrate's surface. This is repeated with each dyne level until the level where the solution does not bead up after two seconds is found (accudynetest.com, 2006). This is the surface tension of the substrate. In the performance of this test on the DuPont DARTEK® film, it was determined that the dyne level of the substrate was 50 dynes/cm. This number was then compared to the surface tension of the ink and determined that corona treatment of the substrate was not needed because the surface tension of the substrate was higher than that of the ink.

Ink

The ink that was used for this experiment was silver RFID antenna flexographic ink. This water-based silver conductive ink is formulated for use in flexographic printing methods and cures through evaporation of solvents over a period of time. The exact ink formulation is not known, but it is primarily composed of a suspension of finely milled silver (Ag) particles in a resin, solvent, and additives solution. Some of the known properties of the ink are that it is about 900cps pre-shear viscosity and is 90% solids

(Williams, 2006). A similar ink could be a water-based metallic ink that consists of pigments derived from micronized flakes of the metal, in this case silver, suspended in an ink vehicle. It is important to note that a property of this type of ink is reactivity. Because the metallic particles are reactive, the vehicles they are suspended in must be inert to prevent a potentially hazardous reaction (Foundation of Flexographic Technical Association, 1999).

Some other important properties of conductive metallic inks are that they attempt to provide a printed surface that can mimic a true metal surface. To do so, the pigments are specially treated and size graded to help determine their orientation in the print ink film. This ensures that the metal flakes are flat and stack on top of each other to promote conductivity; however, this tends to cause problems with cohesion. Another property of metallic inks is that they have a high specific gravity and are prone to settling. This is especially possible in a low viscosity water-based ink used in flexographic printing (Foundation of Flexographic Technical Association, 1999).

To ensure that this ink would adhere to the surface of the substrate used in this experiment, the surface tension of the ink was measured using the Fisher Scientific Surface Tensiomat® 21. The surface tension of the ink was measured at 40 dynes/cm. Therefore, it was determined that the ink did posses sufficient wetting capabilities.

Printing

Print samples were made in the Print Sciences Laboratory (7-A610) at the Rochester Institute of Technology in Rochester, New York using the K Motorized Printing Proofer (as seen in Figure 2 (a), and manufactured by RK Print Coat

Instruments). A patterned anilox plate seen in Figure 2 (b) (Double 8 Wedge Plate – Model EP 5102/2 Rev.K) was used to create the print sample. The anilox plate used had the properties of 150 lines/inch (60 lines/cm) with varying tint patches that have 100-95-90-85-80-75-70-60% density values (RK Print Coat Instruments, n.d.).

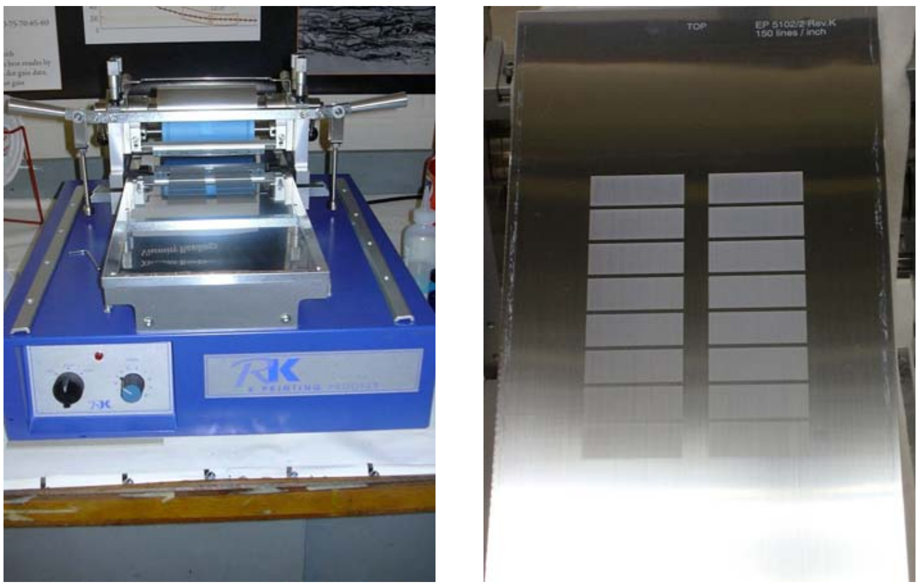

Figure 2 (a), (b): RK K Printing Proofer, EP 5102/2 Rev.K anilox plate

To determine the optimal printing conditions required to replicate printing on press, the researcher made several prints adjusting the impression, stereo, and doctor blade pressure until an even ink-film thickness—the amount of ink transferred to the printing substrate, usually measured in microns—and acceptable visual appearance was achieved. This was determined by creating a *kiss* impression where the least amount of pressure needed to create a consistent image was reached. The researcher evaluated the image at kiss impression to make sure that the image had solid lines with no excess ink deposit. Adjusting the rollers provided more or less ink flow onto the substrate, which caused the ink film thickness as well as the appearance of the print to change. The image that was created from this process was used as a visual reference for comparison when print samples for use in the experiment were created (Figure 3).

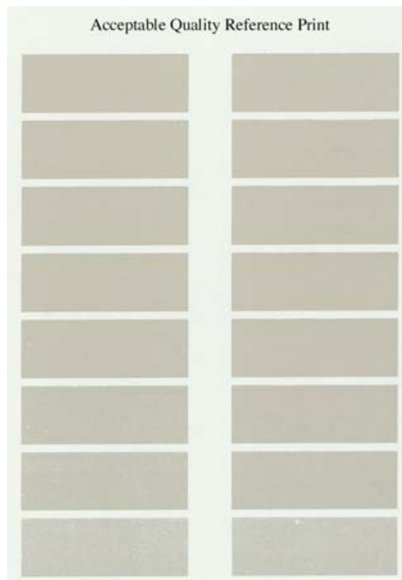

Figure 3: Acceptable quality reference print

The optimal settings used in creating this print were recorded and duplicated to create the print samples for the experiment. These settings include 2.65 for the right and 2.70 for the left of the impression roller, 2.95 for the right and 3.45 for the left of the stereo roller, and 5.70 for the right and 6.36 for the left of the doctor blade. The optimal press speed was determined to be a setting of 4. This process was considered to be the calibration of the proofer.

Print Samples

The print sample was printed five times using the flexographic proofer on the nylon substrate. Five sets of these prints were created for use in the five different inks tests and were exposed to the four environmental conditions, and five prints were created for use as a control set. A set of print samples consists of five prints for the control condition and five prints that will be exposed to an environmental condition. There are 10 prints per set, and there were a total of five sets of print samples created for the four different environmental conditions for a total of 40 prints. Table 2 lists the labels of the prints.

Table 3: Print sample labels used

	Heat Set	Control Set #1	Freeze Set	Control Set #2	Vacuum Set	Control Set #3	Rain Set	Control Set #4
Conductivity Test A	Print 1	Print 1	Print 1	Print 1	Print 1	Print 1	Print 1	Print 1
Density/Color Test B	Print 2	Print 2	Print 2	Print 2	Print 2	Print 2	Print 2	Print 2
Adhesion Test C	Print 3	Print 3	Print 3	Print 3	Print 3	Print 3	Print 3	Print 3
Abrasion Test D	Print 4	Print 4	Print 4	Print 4	Print 4	Print 4	Print 4	Print 4
Creasing Test E	Print 5	Print 5	Print 5	Print 5	Print 5	Print 5	Print 5	Print 5

All prints were allowed a drying period of 24 hours and reacclimation period of one hour before being subjected to environmental conditions and ink testing procedures.

Environmental Exposure

The simulation of typical environmental packaging conditions was performed by creating a set of four 24-hour periods of exposure to a certain condition and one controlled condition. All of the environment simulations, except for the freezing condition, were created in the Print Sciences Laboratory in room A610 of Building 7 at the Rochester Institute of Technology in Rochester, New York.

Control Set

Control sets of prints (five samples) were created for comparison to each of the four environmental condition samples. The samples were printed according to the optimal print settings that were specified in the calibration of the proofer. Each control set was printed concurrently with the environmental set for which it was compared to and was allowed the same curing period (24 hours) as the set of prints for environmental exposure. Also, since each of the environmental exposure samples required an additional 1-hour acclimation period after removal from the environmental condition before conducting testing procedures, this was also allowed for the control samples. The same ink testing procedures performed on the environmental exposure sets were performed on the control set. The notation that was used to identify the control set of prints in the data recording process was CS#1, CS#2, CS#3, and CS#4, each corresponding to one of the four environmental conditions.

Environmental Conditions

Heat Condition (HC). The purpose of creating a heat exposure condition was to subject the print samples to the environment that a package would endure in its lifecycle. Whether through environments it would be exposed to in shipping as a secondary packaging application or environments it would be exposed to as a primary packaging application. The heat exposure was accomplished by mounting the set of five prints to a piece of chip board (Figure 4) and placing them in the Fisher Scientific Isotemp Oven (Figure 5) at a temperature of 140^{o} F (60^{o} C) for a period of 24 hours.

Figure 4: Heat Set print samples mounted to chip board

Figure 5: Heat Set prints placed in Fisher Scientific Isotemp Oven

The prints were then removed and a one-hour acclimation time occurred in which the print samples cooled, after which the ink testing procedures were conducted.

Figure 6: Heat Set samples after removal from environmental condition

Freeze Condition (FC). The purpose of creating a freezing exposure condition was to subject the print samples to the environment that a package would endure in its lifecycle whether through environments it would be exposed to in shipping as a secondary packaging application or environments it would be exposed to as a primary packaging application. The environmental condition was simulated by placing the prints samples in a Ziploc® brand freezer bag and placing them in the researcher's spare GE Spacemaker® 4.3.0 Cu. Ft. Compact Refrigerator/Freezer in the freezer compartment at a temperature of 15^{o} F (-9.4^{o} C) which met the conditions for freezing temperatures (32^{o} F or 0^{o} C). After a period of 24 hours, the print samples were removed from the freezer and a 1-hour acclimation period began. After this period the print samples were subjected to ink testing procedures.

<u>Vacuum Condition (VC).</u> The purpose of creating a vacuum exposure condition was to subject the print samples to the environment that a package would endure in its lifecycle whether through environments it would be exposed to in shipping as a secondary packaging application or environments it would be exposed to as a primary packaging application. This condition was created by sealing the five print samples in a Space Savers (Model 1AT91208 by Space Bag®) 13.75" x 19.5" storage bag for 24 hours. The vacuum seal was created by connecting a standard household upright vacuum to the valve (Figure 7). When the upright vacuum was turned on, the air within the bag was removed and a vacuum environment was created.

Figure 7: Vacuum environment created with the use of a household vacuum

After a period of 24 hours the print samples were removed from the vacuum-sealed bag and a one-hour acclimation period began. After this period the print samples were subjected to ink testing procedures.

Rain Condition (RC). The purpose of creating a rain exposure condition was to subject the print samples to the environment that a package would endure in its lifecycle whether through environments it would be exposed to in shipping as a secondary packaging application or environments it would be exposed to as a primary packaging application. This condition was achieved by attaching the samples to a plastic backing board and standing this backing board up in a water basin. Tap water with a temperature of 45^{o} F (7.2^{o} C) was circulated through a sprinkler head attached to a half-inch plastic hose connected to a TEEL open-air submersible pump. The hose was suspended 12 inches above the backing board and directionally aimed so that the spray from the sprinkler head completely covered the prints (Figure 8).

Figure 8: Rain Condition environment

This was performed for a period of 24-four hours at which point the samples were removed and a one-hour acclimation period in which the sample were allowed to air-dry occurred. After which the print samples were subjected to the ink testing procedures.

Figure 9: Rain Set prints after removal from environmental condition

Figure 10: Rain Set print after one hour acclimation period

Ink Testing Procedures

Several ink testing procedures have been established within the print industry to test the properties of inks under many common end-use conditions. These tests are used to evaluate ink requirements and performance under a given set of conditions (Foundation of Flexographic Technical Association, 1999). The purpose of this experiment was to test the performance of a silver conductive water-based ink under certain common environmental conditions that flexible substrates, such as polyamides, are subjected to. Therefore, five tests were selected: conductivity, density and color, adhesion, abrasion, and creasing.

Conductivity

A Model # 22-806 RadioShack digital multimeter was used to measure electrical resistance of the print samples. To determine the conductivity of the tint patches—the inverse measurement of conductivity—resistance was measured in ohms/square and was performed by measuring the resistance over a one-centimeter distance. Five different measurements were taken on various locations of each of the patches and were averaged. These averages were recorded for both the control and environmental conditions and compared.

Density and Color

Density and color was measured using an X-Rite DTP 22 Model handheld spectrophotometer. A spectrophotometer was the chosen measuring device because the researcher wanted to collect both density information as well as the color data of the ink. A spectrophotometer functions by measuring the color spectrum of a sample by reporting the reflectance or transmittance of a sample. The spectral data can then be used to determine the LAB values which are needed to evaluate the color of the ink (Sharma, 2004).

An average of five density and LAB values were taken on each sample exposed to an environmental condition from various points on each tint patch and recorded. Density with respect to transmittance, is the ratio of incidental light measured to the amount of light transmitted. With regards to reflection, it is the ratio of incidental light measured to the amount of light reflected (Sharma, 2004). LAB values are a set of measurements that are taken from a sample print that are used in determining color. L* is a measure of lightness, a* is a measure of the position of the color on the red-green axis, and b* is the measure of the position of the color on the yellow-blue axis. Through the use of these three values, a person is able to map the color in a three-dimensional space and give it a quantitative value (Sharma, 2004).

These averages were then compared to those of the control sample, and the Delta E value for both the control and environmental condition were calculated and compared. The purpose of calculating the Delta E value was to compare the change in color from the control sample to that of the environmentally exposed sample to determine if the exposure had an effect on the color of the ink. To calculate the Delta E value, the LAB measurements of both the control sample and the chosen environmental sample were obtained, and the number between the two samples was calculated. This resulted in a value of Delta E. The greater the Delta E value, the greater difference in color there is for the sample (Sharma, 2004).

Adhesion

The adhesion of the ink for both the control sample and the environmental condition sample were tested. The print samples were secured to the surface of a table. A piece of 1-inch by 2-inch pressure-sensitive tape (3M-610) was applied to the print sample (Figure 11). A rubber roller was used to ensure that there were no air bubbles between the tape and the substrate (Figure 12). The tape was then pulled from the print sample at a 150^{o} angle, and the resistance of the sample was measured after each removal of the tape (Figure 13).

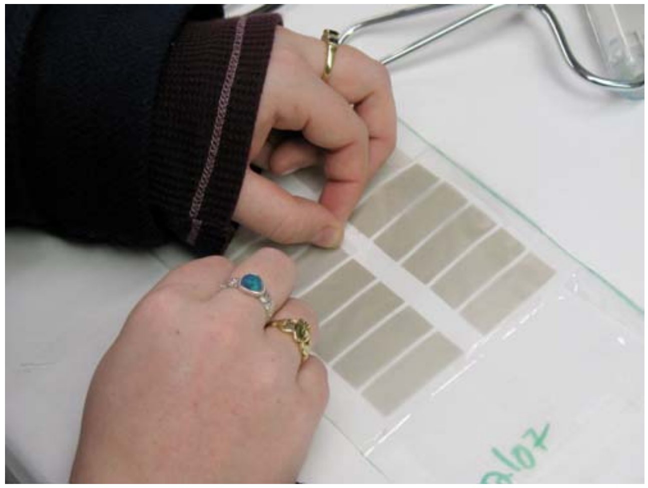

Figure 11: Print sample attached to table surface while tape is placed on to printed patch

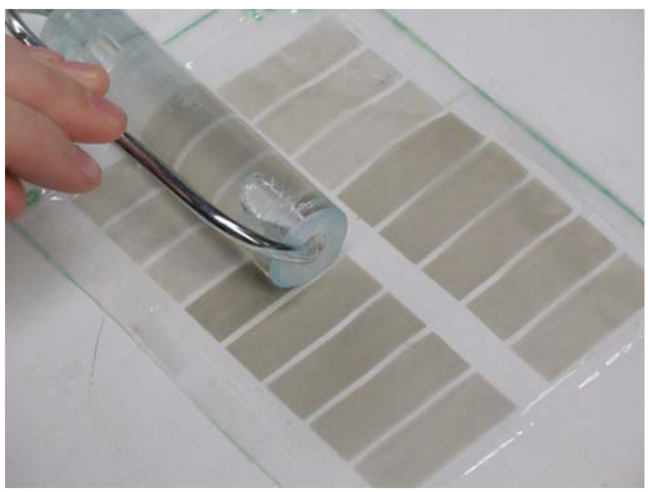

Figure 12: Use of rubber roller to remove air bubbles from under tape

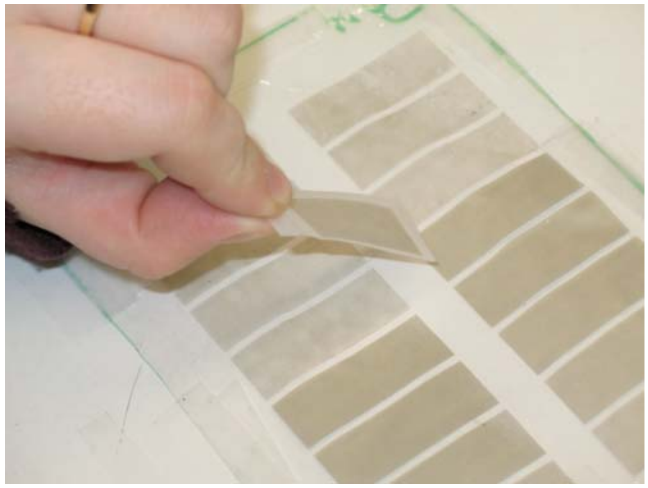

Figure 13: Removal of tape from print sample

The number of adhesive pulls it took to cause conductivity failure was recorded. The average of these values was compared with the average of the control set to determine whether exposure to a certain environmental condition had an effect on the adhesion performance of the ink.

Abrasion

Abrasion testing was performed in the fashion of the Sutherland rub test that has been established as a standard for testing ink adhesion of flexographic inks. The purpose of this test was to make sure that an antenna printed on a package could withstand handling between the press and point of sale, which includes typical shipping environments (Foundation of Flexographic Technical Association, 1999). This was performed by attaching the print sample print-side up to an inclined plane at a 20^{o} angle. A piece of nylon substrate was attached to the bottom of a 500g weight that was released at the top of the inclined plane 10 times (Figure 14) after which a measurement of resistance was taken of each tint patch (Figure 15).

Figure 14: Nylon covered weight being released down inclined plane

Figure 15: Use of digital multimeter to obtain resistance measurement for each patch

This was repeated until the tint patch exhibited an infinite measurement of resistance. This indicated that the patch was no longer conductive. The number of passes it took to achieve this status for each patch of the environmental condition sample was recorded and compared to the number recorded for the control condition.

Creasing

Crease testing was conducted by making a crease on each of the tint patches. Each crease was made by folding the print sample once (Figure 16) and placing a weight on it for a period of 10 minutes (Figure 17). The resistance was measured and recorded. Each tint patch of the print sample was then unfolded/refolded with the weight replaced on the sample for 10 minutes until the measurement of the patch indicated conductivity failure.

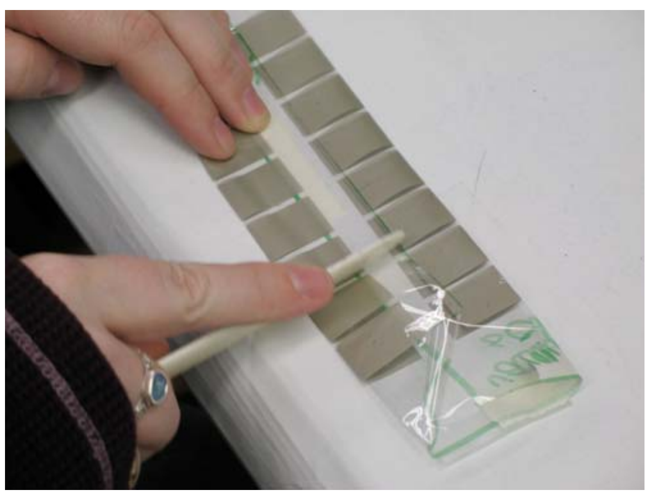

Figure 16: Creasing of print sample

Figure 17: Placement of weights on print sample

The number of times the samples were creased was recorded for both the control and the environmental condition sample. The average of these values was compared to determine if the environmental exposure had an effect on the integrity of the ink.

Data Analysis

A simple statistics model was used in evaluation of the data set. Averages of results for each print sample of the individual environmental conditions were calculated for each of the tests performed. These calculations were then compared to that of the control environment to analyze the results.

Limitations

One of the limitations of this experiment was that a limited number of samples were tested. For the testing used in this experiment to be statistically significant, a minimum of 1,200 print samples should be tested. 60 samples (30 control, 30 exposure) per the four environmental conditions per the five ink tests is the minimum desired sample size for statistical significance (60 prints * 4 environmental conditions * 5 ink tests = 1,200 total prints). Testing of this scale was not possible because of the limitations of the scope of this project. Another limitation was that the environmental conditions that were set up for this experiment are simulations of a real-world environment. Results would be more accurate if the experiment was tested over a period of time in the actual environments described.

Chapter 6

Results

Control Sets

Treatment of Control Sets

For each ink-testing procedure performed, a comparison control set was printed for each of the four environmental conditions. In addition to comparison against the set of prints exposed to the environmental conditions, the consecutive control sets (#1–4) were compared to each other. The reason for comparing control sets is because of inconsistent measurements particularly for the 80–70% tint patches. The results (Figures 18 – 22) of this comparison of consecutive controls sets for each ink test are indicated in.

Discussion of Treatment of Control Sets

<u>Conductivity.</u> In Figure 18, the resistance measured in ohms/cm was compared between control sets #1–4 for each of the tint patches. In comparison of these measurements, it can be seen that each successive control set provided more resistance than the previous.

<u>Density.</u> In Figure 19, the density measurement was compared between control sets #1–4 samples for each of the tint patches. This graph indicates that the control set density measurements differed by 0.021 for the 75% and 70% tint patch and 0.038 for the 60% tint patch.

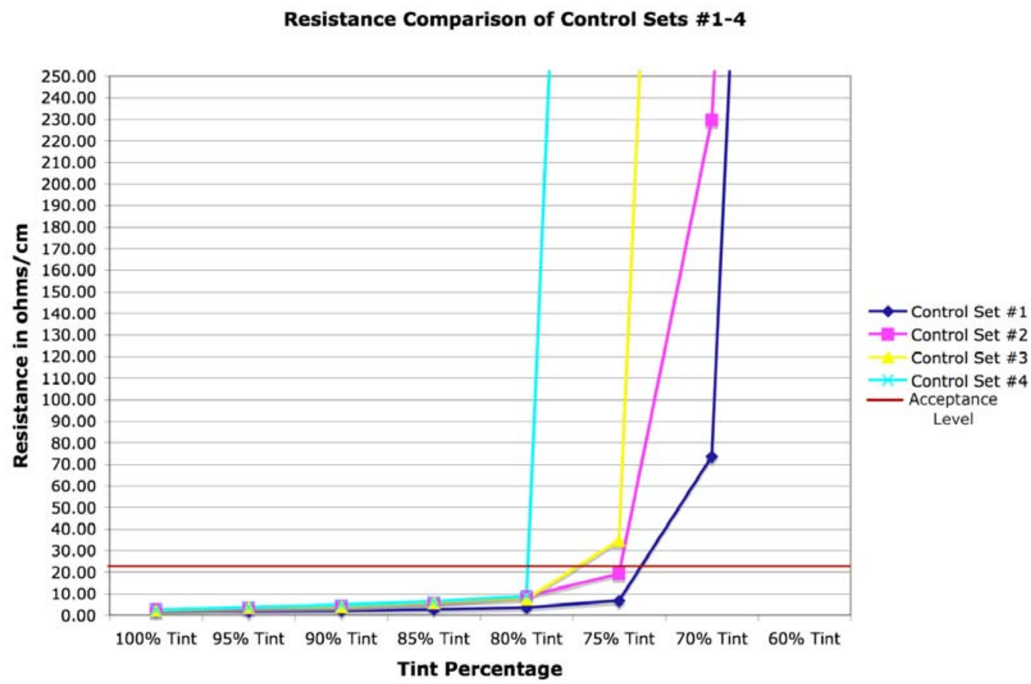

Figure 18: Resistance Comparison of Control Set #1-4

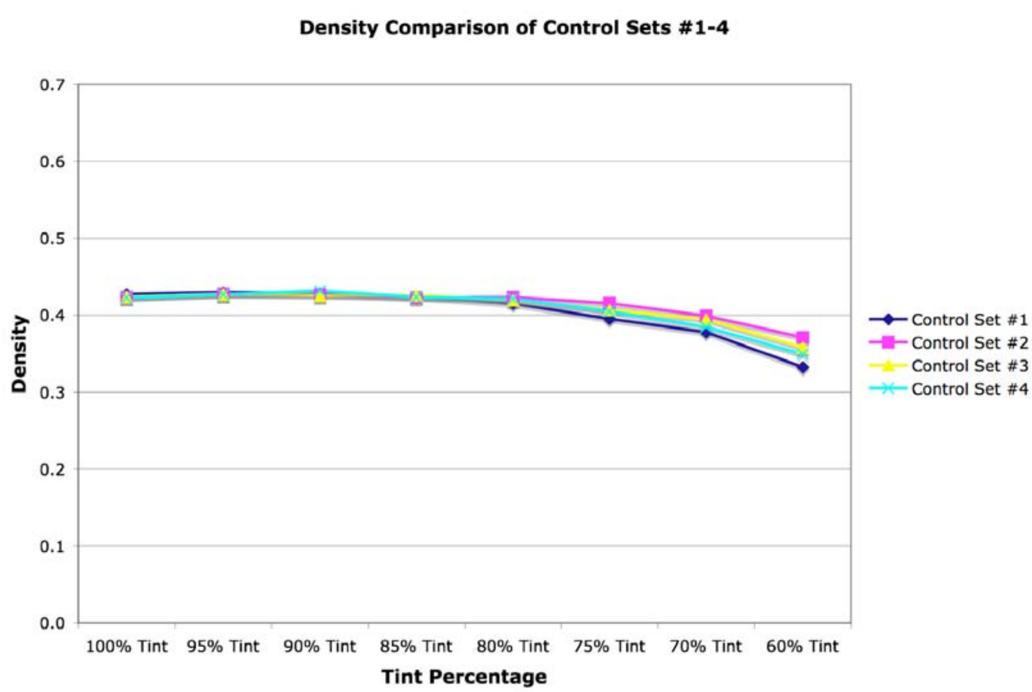

Figure 19: Density Comparison of Control Sets #1-4

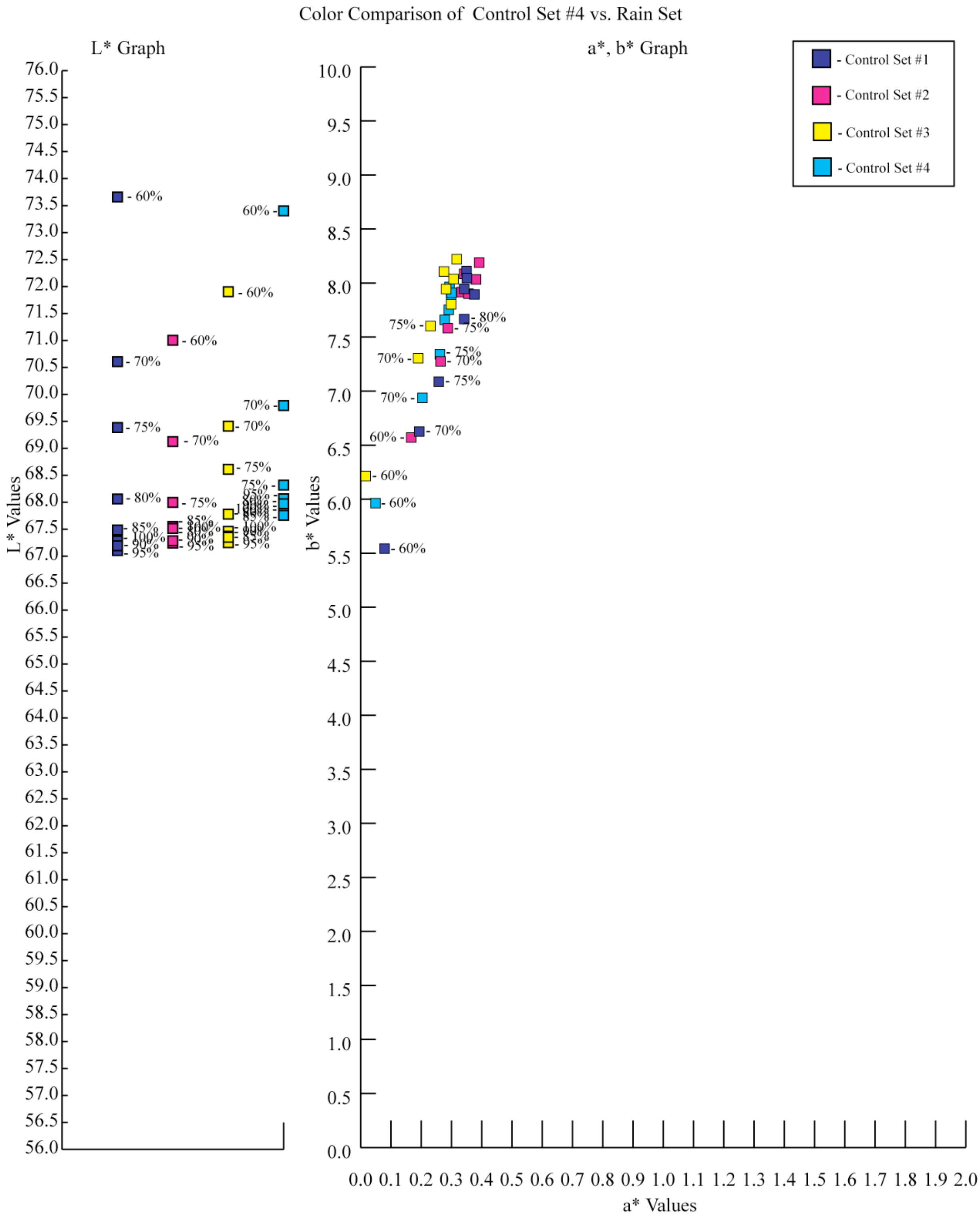

Figure 20: L* and a*, b* Comparison of Control Sets #1-4

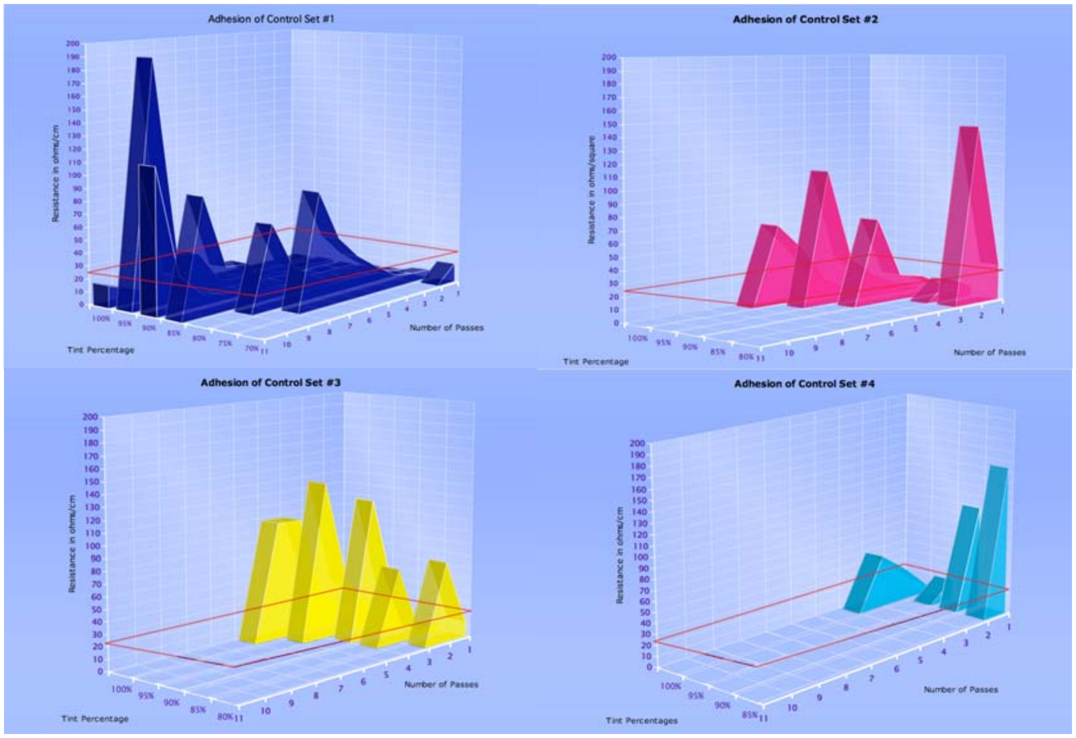

Figure 21: Adhesion Comparison of Control Sets #1-4

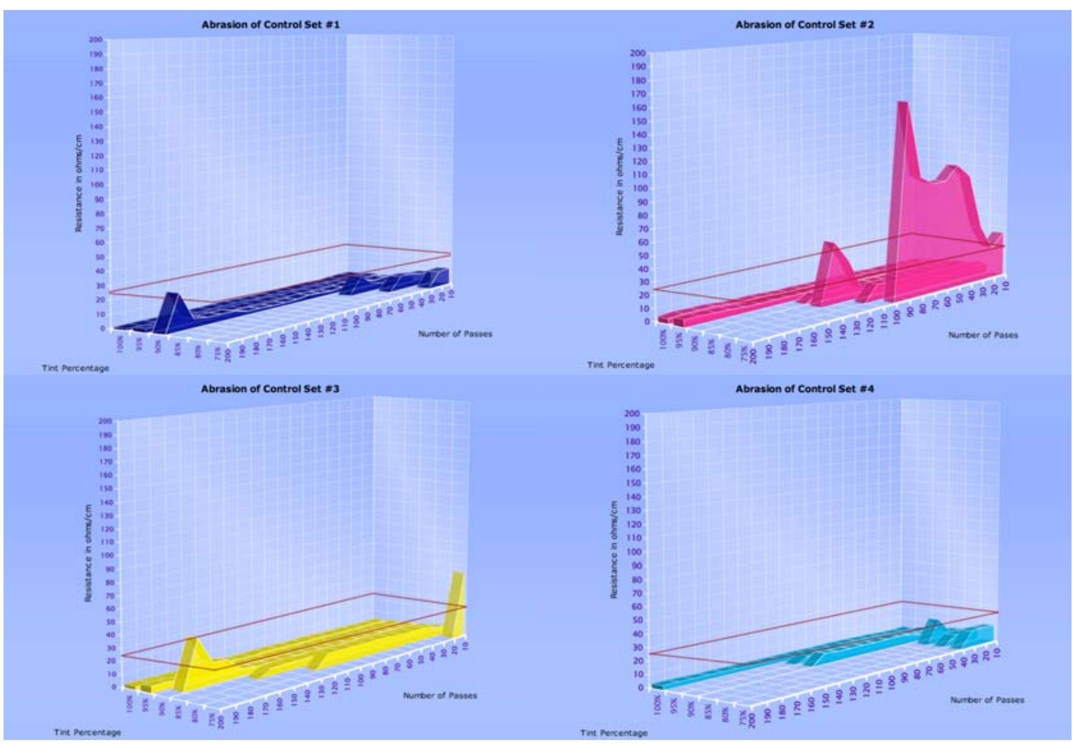

Figure 22: Abrasion Comparison of Control Sets #1-4

Color. In Figure 20, the L* values indicate that there was a slight difference in the lightness of the control sets. A difference in the a*, b* values of less than 0.5 for each tint patch, indicated that there was not a significant shift in the color space of the control sets.

Adhesion. Figure 21 shows the adhesion of control sets #1–4. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. Each successive control set performed more poorly than the preceding. Control Set #1 conductivity dropped off after two passes on the 70% tint patch; Control Set #2 dropped off after three passes on the 80% tint patch; Control Set #3 dropped off after three passes on the 80% tint patch also but recorded much higher resistance levels than that of Control Set #2. Control Set #4 dropped off after two passes on the 85% tint patch. This indicates that there was a negative effect on the successive print performances of each control set.

Abrasion. Figure 22 shows the adhesion of control sets #1–4. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the acceptable level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. This figure indicates there was not a significant difference in abrasion properties of the control sets. Each one exhibited a drop off in conductivity at the 75% tint patch varying from 20 to 100 passes required to produce an infinite resistance measurement.

Test A – Conductivity

The conductivity test was performed using a digital multimeter on which measurements of resistance were recorded in ohms/square, five times at five different points on the each of the tint patches (100-95-90-85-80-75-70-60). The means of the measurements (Figures 23-26) were then calculated and graphed.

Discussion of Conductivity

<u>Heat Condition.</u> In Figure 23, the resistance measured in ohms/cm was compared between the Control Set #1 and Heat Set samples for each of the tint patches. This comparison provides several indications. For the Control Set, it can be seen that the conductivity level dropped off after the 70% tint patch. The Heat Set conductivity dropped off at the 80% tint patch. The measurements for the 100% patch through the 85% patch appeared to be uneffected by exposure the environmental condition. The conductivity level of the samples exposed to the Heat Condition appeared to be uneffected for the 100–85% tint percentage; however the conductivity level was definitely effected by exposure to the condition for the 80–70% patches. For both, the

60% patch measured a greater resistance to conductivity than permitted by the acceptable level for antenna production previously established.

Freeze Condition. In Figure 24, the resistance measured in ohms/cm was compared between the Control Set #2 and Freeze Set samples for each of the tint patches. The Control Set conductivity level dropped off after the level of the 70% tint, which is consistent with the measurement from Control Set #1. The Freeze Set sample conductivity also dropped off after the 70% tint level, however the resistance measurement for the Freeze Set at the 70% tint level was 36.22 ohms/cm. The Control Set measurement is 229.70 ohms/cm at this level. This indicates that exposure to the freeze condition appeared to slightly improve the conductivity for the 80–70% tint. Consistent with the results of Control Set #1, the 60% tint patch was not conductive.

Vacuum Condition. In Figure 25, the resistance measured in ohms/cm was compared between the Control Set #3 and Vacuum Set samples for each of the tint patches. The conductivity dropped off after the 75% tint patch for both the Control and Vacuum sets. For the 100–90% tint patches, the environmental condition did not appear to have an effect on the conductivity level. It cannot be determined if the condition had an effect on conductivity for the 85–75% tint patches because for the 85% and 80% patches the Vacuum Set produced a higher resistance measurement. However, for the 75% patch, it produced a significantly lower resistance measurement than that of the Control Set.

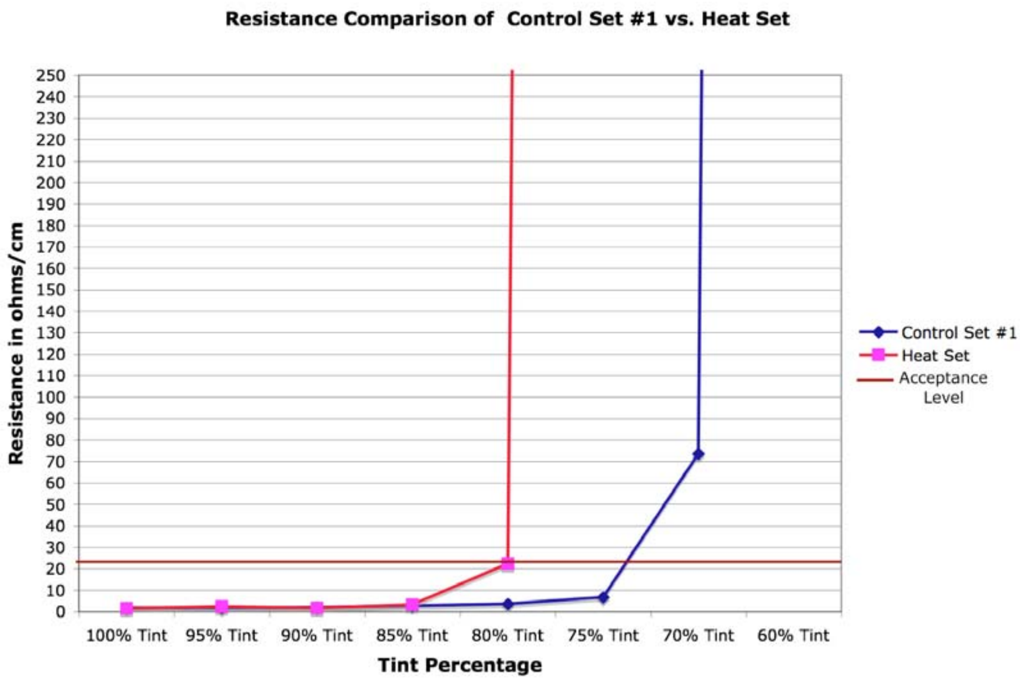

Figure 23: Resistance Comparison of Control Set #1 vs. Heat Set

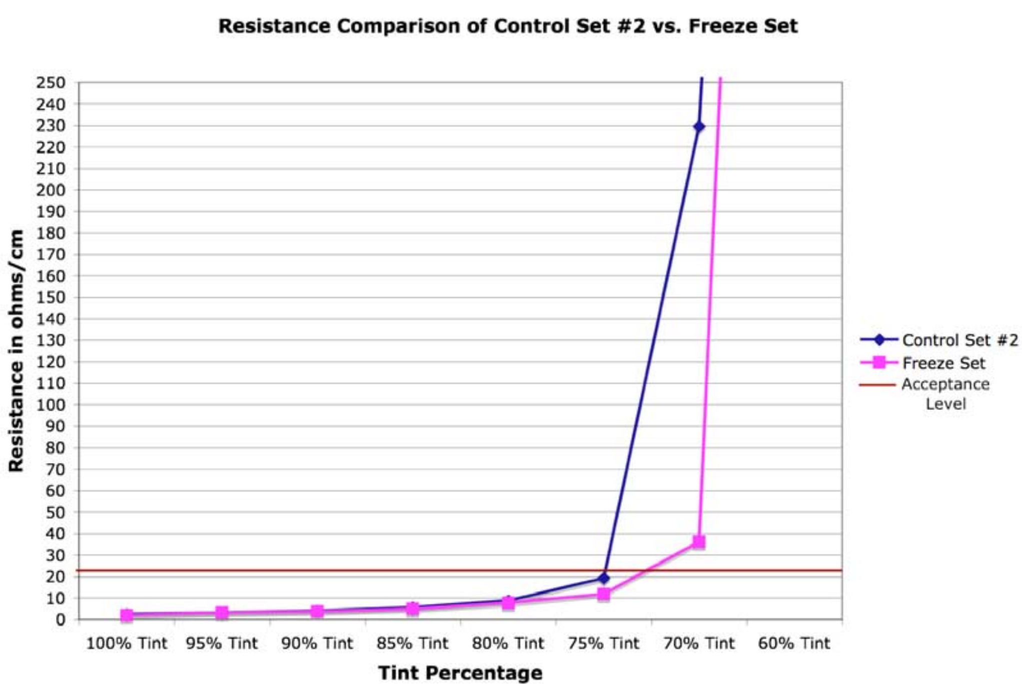

Figure 24: Resistance Comparison of Control Set #2 vs. Freeze Set

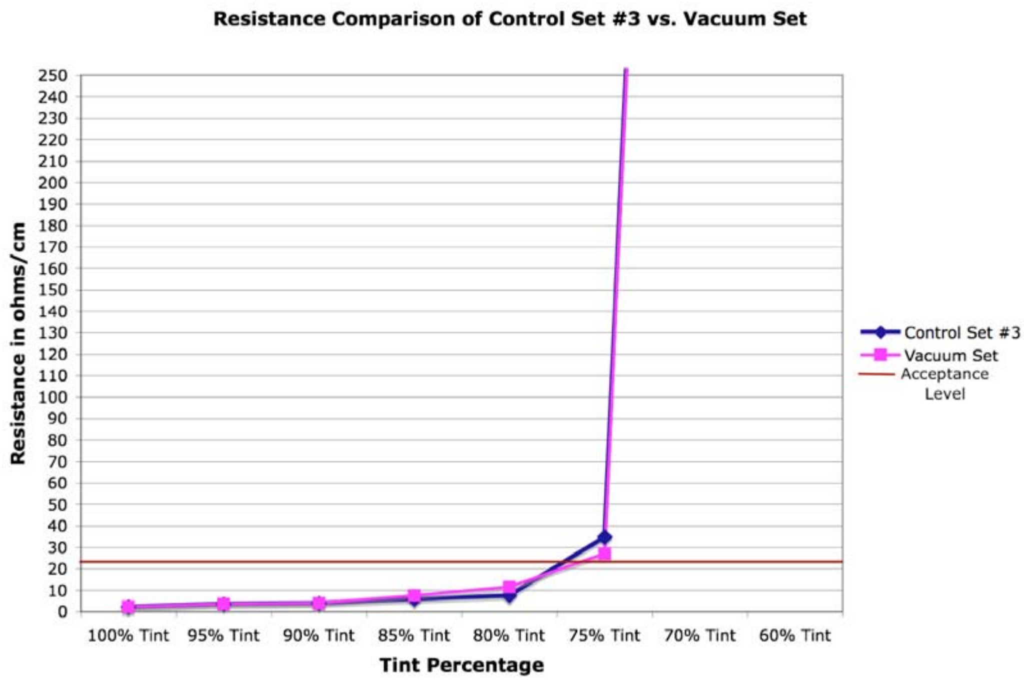

Figure 25: Resistance Comparison of Control Set #3 vs. Vacuum Set

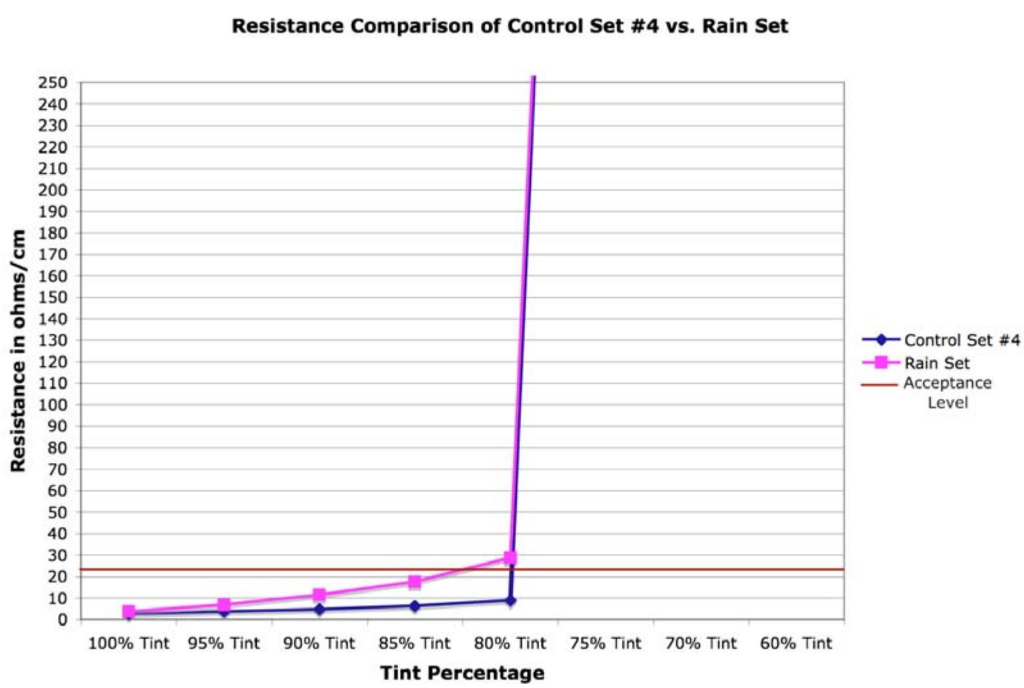

Figure 26: Resistance Comparison of Control Set #4 vs. Rain Set

Rain Condition. In Figure 26, the resistance measured in ohms/cm was compared between the Control Set #4 and Rain Set samples for each of the tint patches. Both the Control Set and the Rain Set samples dropped off in conductivity level after the 80% tint patches. The 100–80% tint patches all produced a resistance measurement that was significantly higher than that of the Control Set indicating that exposure to the Rain Condition had an effect on the conductivity level of the print samples.

Test B – Density and Color

Density Test

The density test was performed using a handheld spectrodensitometer in which measurements were taken five times at five different points on the each of the tint patches (100-95-90-85-80-75-70-60). The means of the measurements were then calculated and graphed (Figures 27–30).

Discussion of Density

Heat Condition. In Figure 27, the density measurement was compared between the Control Set #1 and Heat Set samples for each of the tint patches. For every tint patch 100–60%, the density measurements of the Heat Set are higher than those of the Control Set. This indicates that exposure to the heat condition does have an effect on the density of the print samples.

Freeze Condition. In Figure 28, the density measurement was compared between the Control Set #2 and Freeze Set samples for each of the tint patches. With the exception of the 100% tint patch, the Freeze Set produced density measurements that were slightly lower than the Control Set. However, these differences were not great enough to indicate that there was any effect of exposure to the freeze condition on the density levels of the print sample.

Vacuum Condition. In Figure 29, the density measurement was compared between the Control Set #3 and Vacuum Set samples for each of the tint patches. Only three of the tint patches (85%, 70% and 60%) had a slightly lower density than that of the Control Set. Five of the tint patches (100-90%, 80% and 75%) had density measurements that did not differ significantly from the Control Set therefore; there was no indication as to whether the vacuum condition had an effect on the density of the print samples.

Rain Condition. In Figure 30, the density measurement was compared between the Control Set #4 and Rain Set samples for each of the tint patches. For each tint patch there did not appear to be a significant change in density measurements. This indicates that the rain condition did not appear to have had an effect on the print samples.

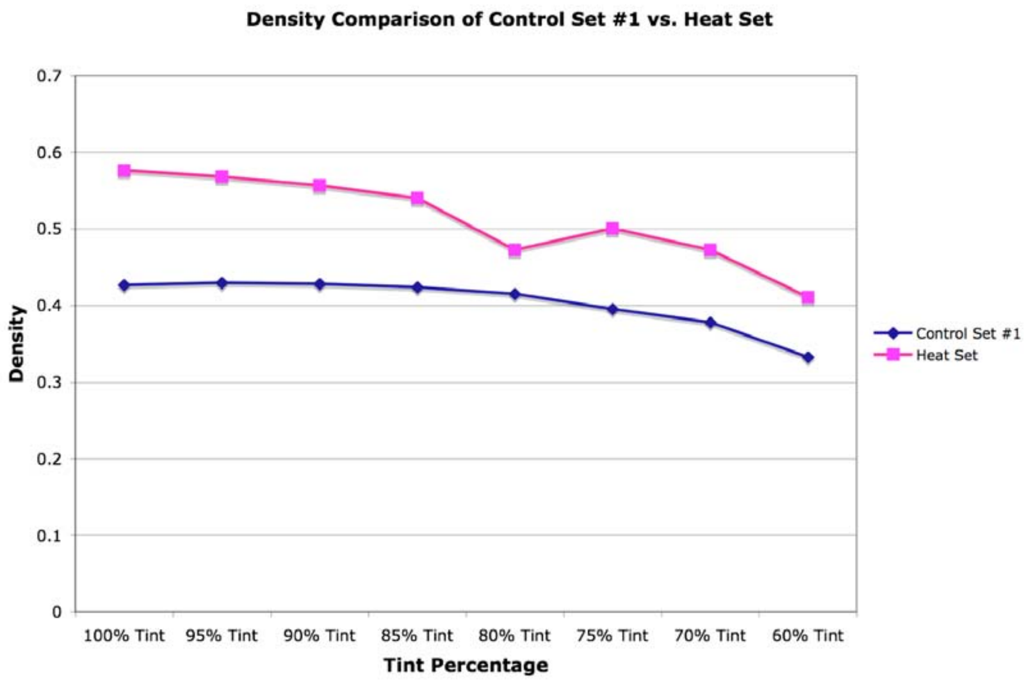

Figure 27: Density Comparison of Control Set #1 vs. Heat Set

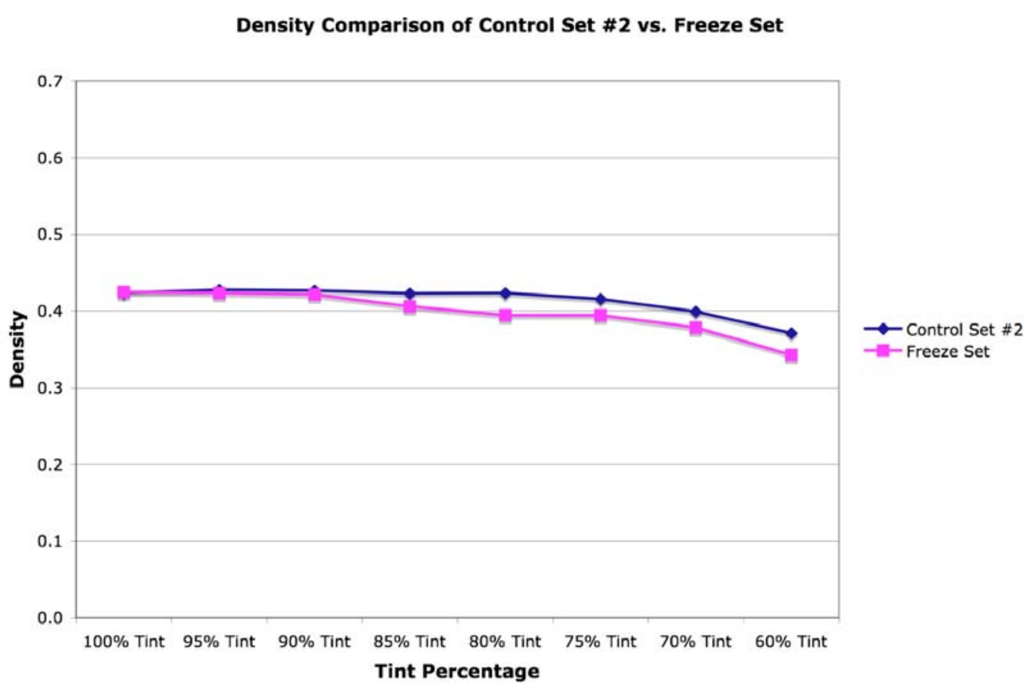

Figure 28: Density Comparison of Control Set #2 vs. Freeze Set

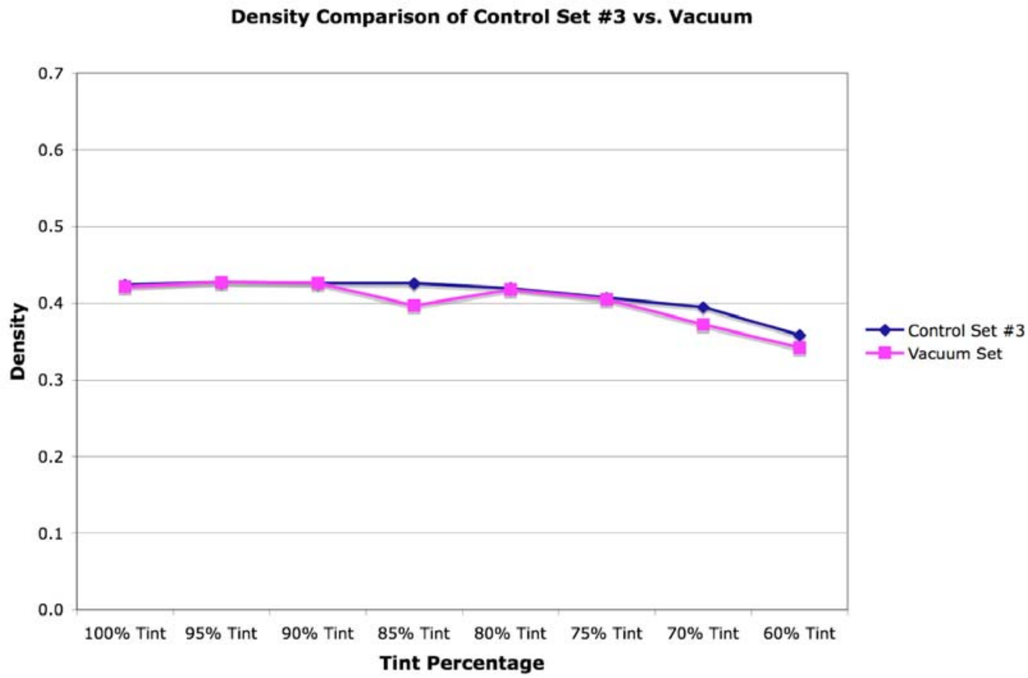

Figure 29: Density Comparison of Control Set #3 vs. Vacuum Set

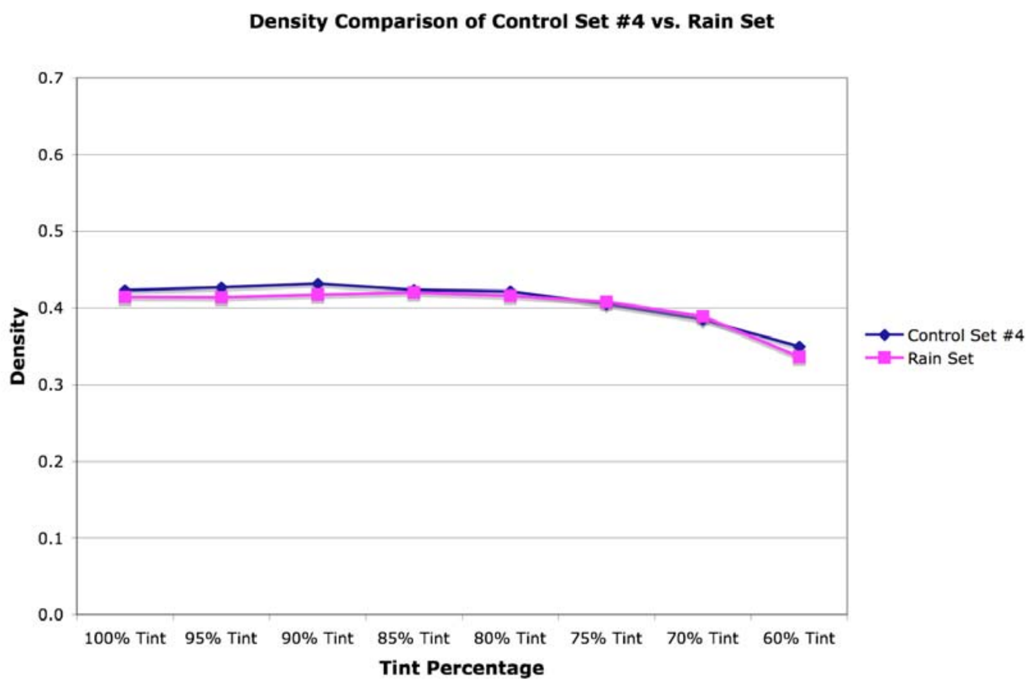

Figure 30: Density Comparison of Control Set #4 vs. Rain Set

Color Test

The color test was performed using a handheld spectrodensitometer in which measurements were taken five times at five different points on the each of the tint patches (100-95-90-85-80-75-70-60). The means of the measurements were then calculated and are represented in figures 31–34.

Discussion of Color Test

Heat Condition. In Figure 31, the L* values indicate that there was a significant shift in lightness from the Control Set to the Heat Set. The a*, b* values indicated that there was a significant shift in the color space of the Heat Set ink to a more blue (b* axis) and red (a* axis) hue than that of the Control Set. This indicates that exposure to the heat condition produced a significant shift in LAB values.

Freeze Condition. In Figure 32, the L* values indicate that there was not a significant difference in lightness of the Control Set and Freeze Set. The a*, b* values have shown that there was not a significant shift in the color space of the Control Set to the Freeze Set. This indicates that the freeze condition did not have a significant effect on the color space of the print sample.

Vacuum Condition. In Figure 33, the L* values indicate that there was not a significant difference in lightness of the Control Set and Vacuum Set. The a*, b* values have shown that there is not a significant shift in the color space of the Control Set to the Vacuum Set. This indicates that the vacuum condition did not have a significant effect on the color space of the print sample.

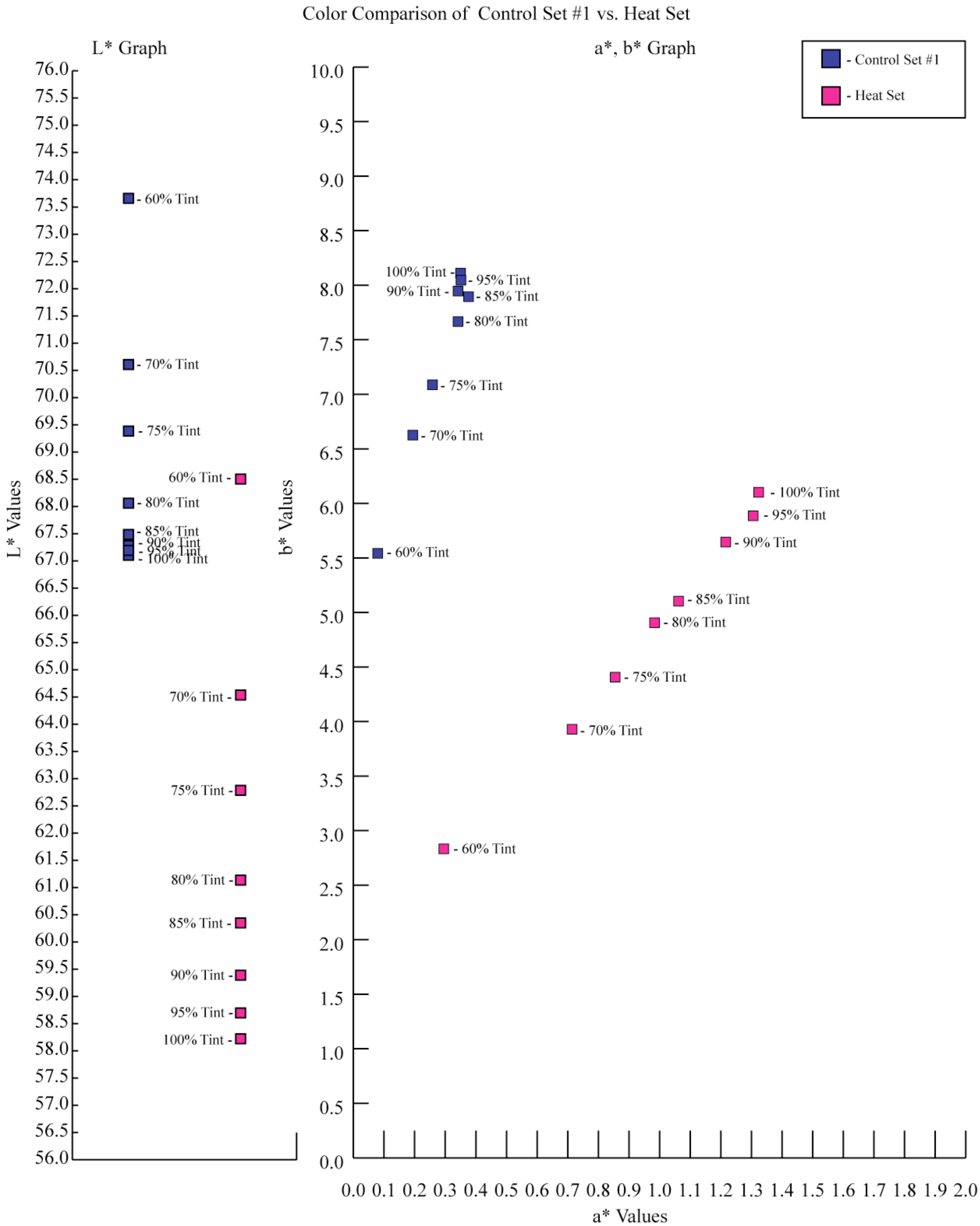

Figure 31: L* and a*, b* Comparison of Control Set #1 vs. Heat Set

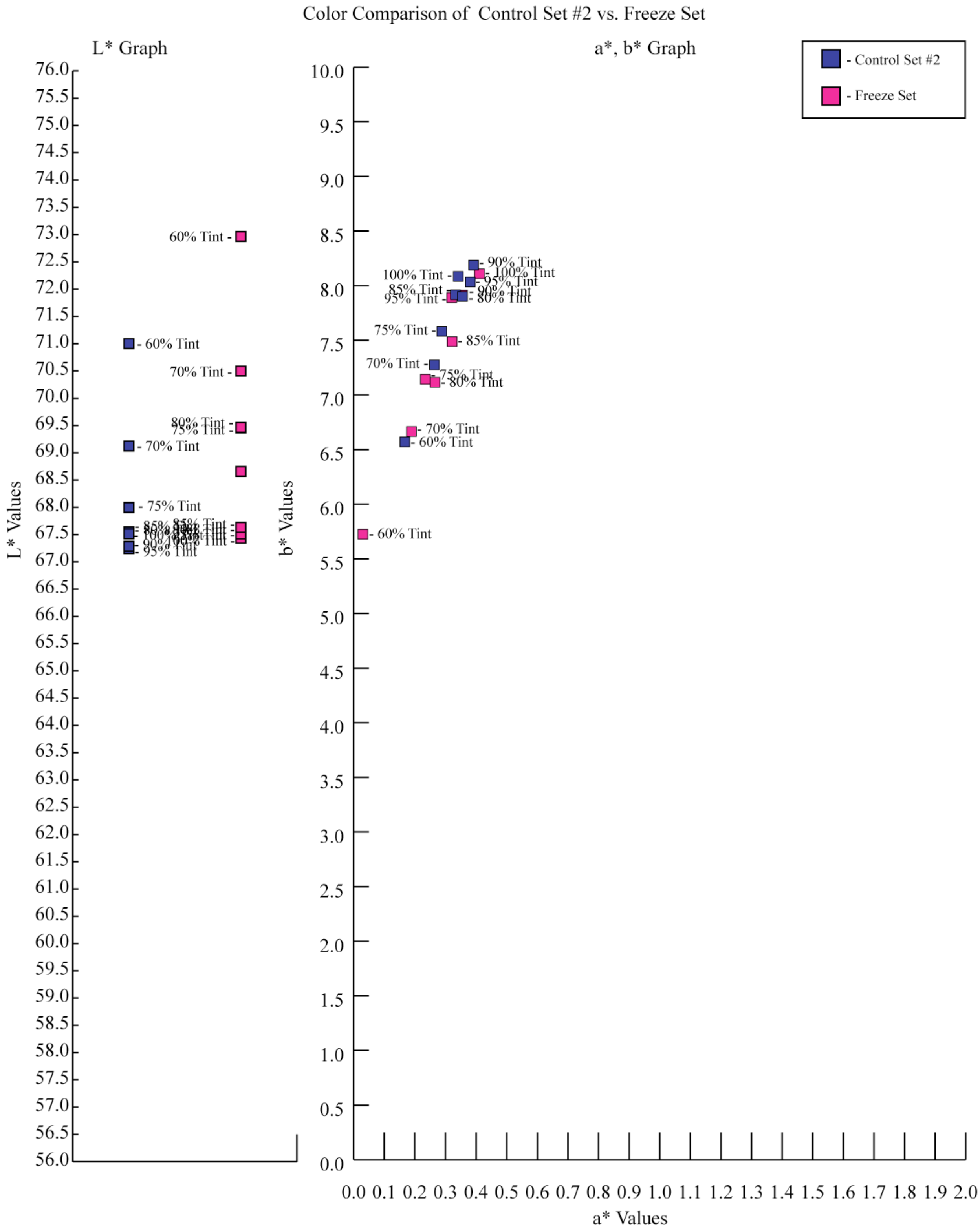

Figure 32: L* and a*, b* Comparison of Control Set #2 vs. Freeze Set

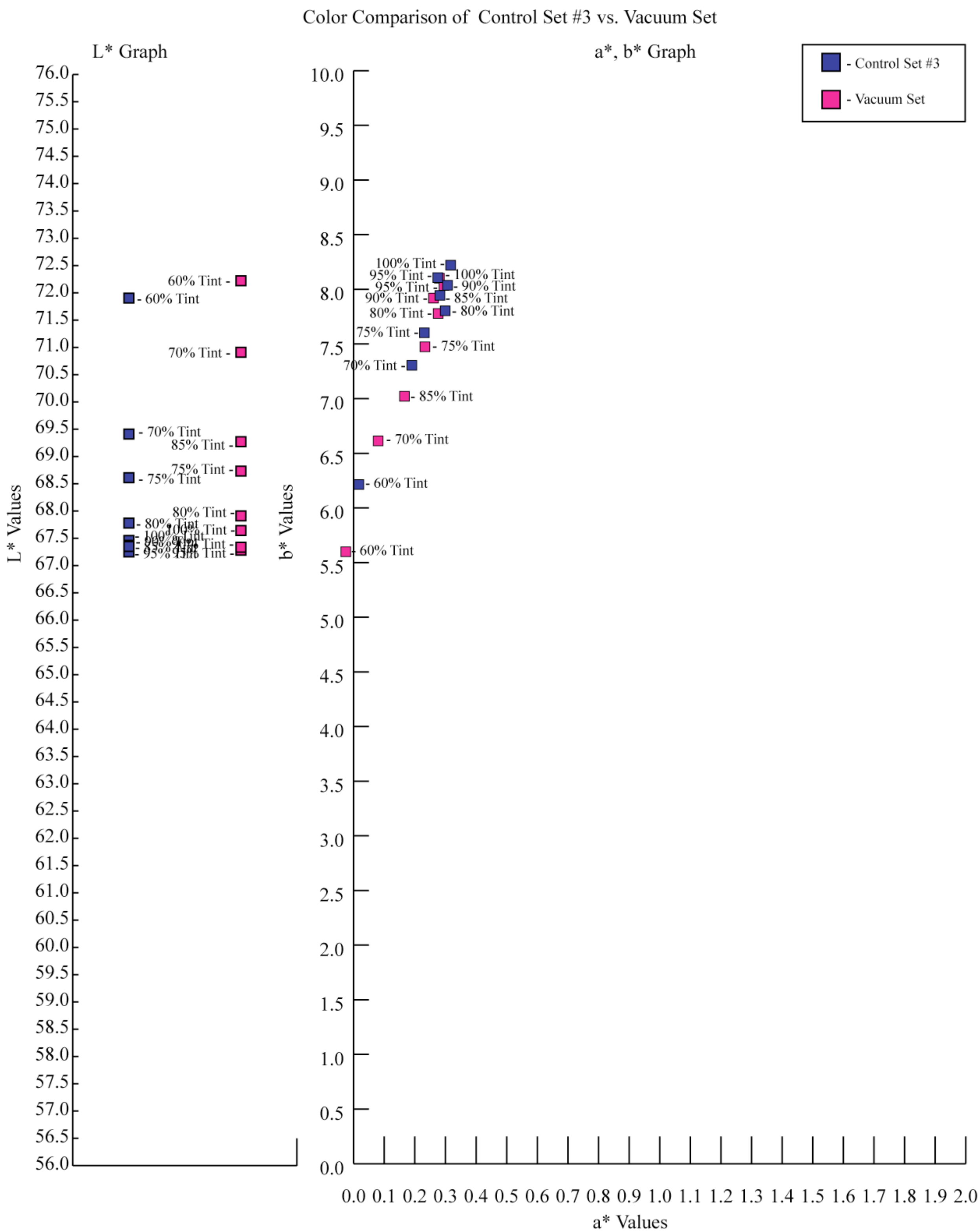

Figure 33: L* and a*, b* Comparison of Control Set #3 vs. Vacuum Set

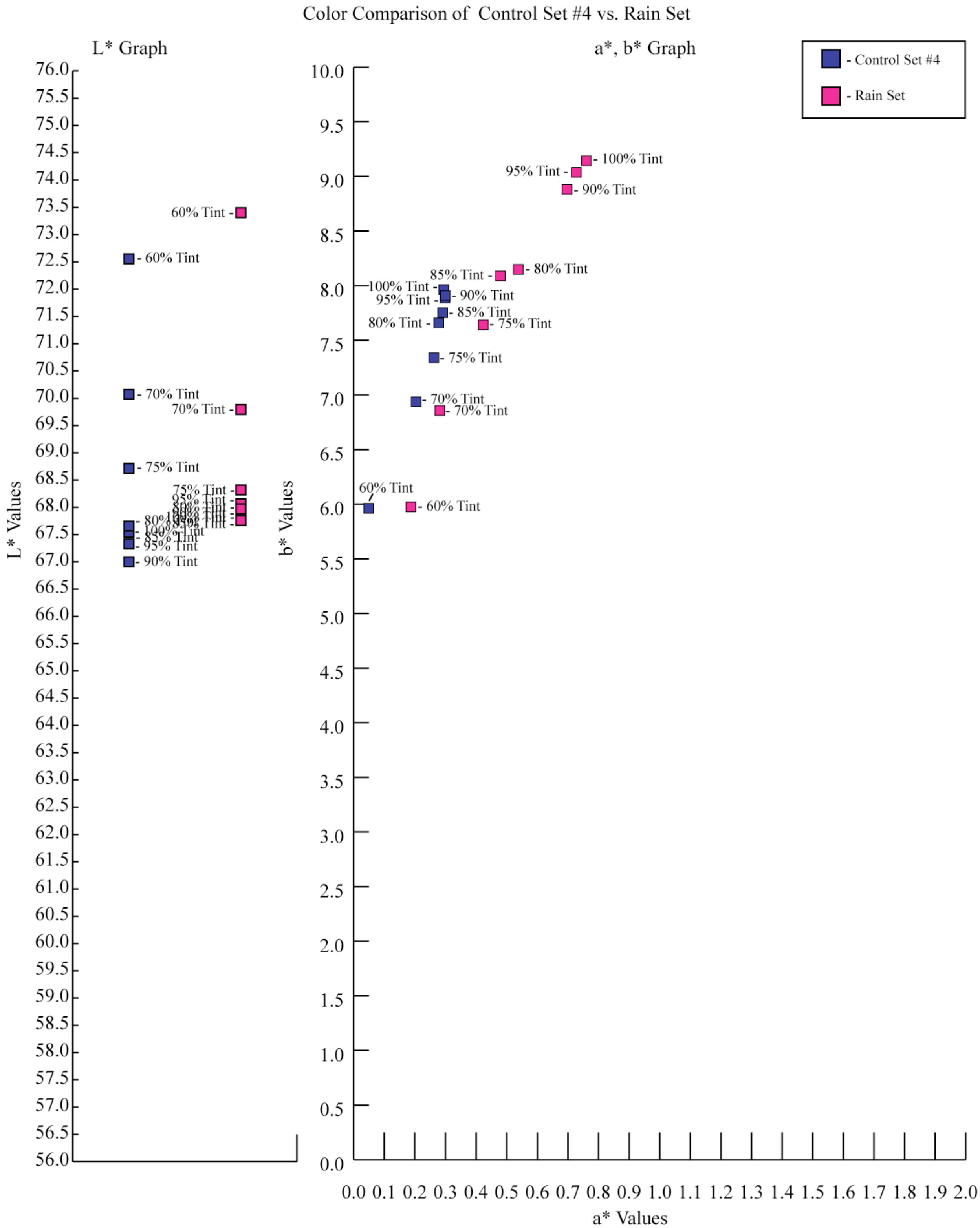

Figure 34: L* and a*, b* Comparison of Control Set #4 vs. Rain Set

Rain Condition. In Figure 34, the L* values indicate that there a slight shift in lightness of the Rain Set. Also, the a*, b* values have shown that there was a slight shift in the color space of the Rain Set. This indicates that the rain condition has a slight effect on the color of the print samples.

Delta E Comparison

Table 2 shows the change in color for the control sets and their respective environmental conditions for each tint percentage patch. This table indicates that the greatest difference in color was produced by exposure to the heat condition. Most of the Delta E measurements for all of the conditions fall within the commonly accepted level of a Delta E value of 4–8 that is used in print production (Sharma, 2004).

Table 4: Delta E values for Control Sets vs. Environmental Condition Sets

Tint Percentage	**CS #1 and HS Delta E**	**CS #2 and FS Delta E**	**CS #3 and VS Delta E**	**CS #4 and RS Delta E**
100%	9.331	0.114	0.219	1.298
95%	8.730	0.310	0.084	1.431
90%	8.140	0.443	0.130	1.365
85%	7.691	1.187	2.135	0.444
80%	7.482	2.095	0.138	0.637
75%	7.147	1.533	0.182	0.524
70%	6.664	1.490	1.655	0.370
60%	5.762	2.143	0.694	0.857

Test C– Adhesion

The adhesion test was performed using the pressure sensitive tape adhesion testing previously described. The number of passes it took to cause the sample to provide an infinite resistance measurement was recorded, and the mean of these values for both the environmental set and control set were graphed (Figures 35–48) to determine whether exposure to a certain environmental condition had an effect on the ink of the printed sample.

Discussion of Adhesion

Heat Condition. Figure 35 compares the adhesion of Control Set #1 and the Heat Set. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the acceptable level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. The conductivity of the Heat Set dropped off after the 90% tint patch, while the Control Set dropped off after the 70% tint patch. Also, the number of passes it took to break the conductivity of the Heat Set was significantly less than that of the Control Set. This shows that the heat condition had a negative effect on the adhesion properties of the print samples when compared to the Control Set.

Freeze Condition. Figure 36 compares the adhesion of Control Set #2 and the Freeze Set. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the acceptable level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. The conductivity of the Freeze Set dropped off after the 75% tint patch, while the Control Set dropped off after the 80% tint patch. Also, the number of passes it took to break the conductivity of the Freeze Set was more than that of the Control Set. This shows that the freeze condition had a positive effect on the adhesion properties of the print samples when compared to the Control Set.

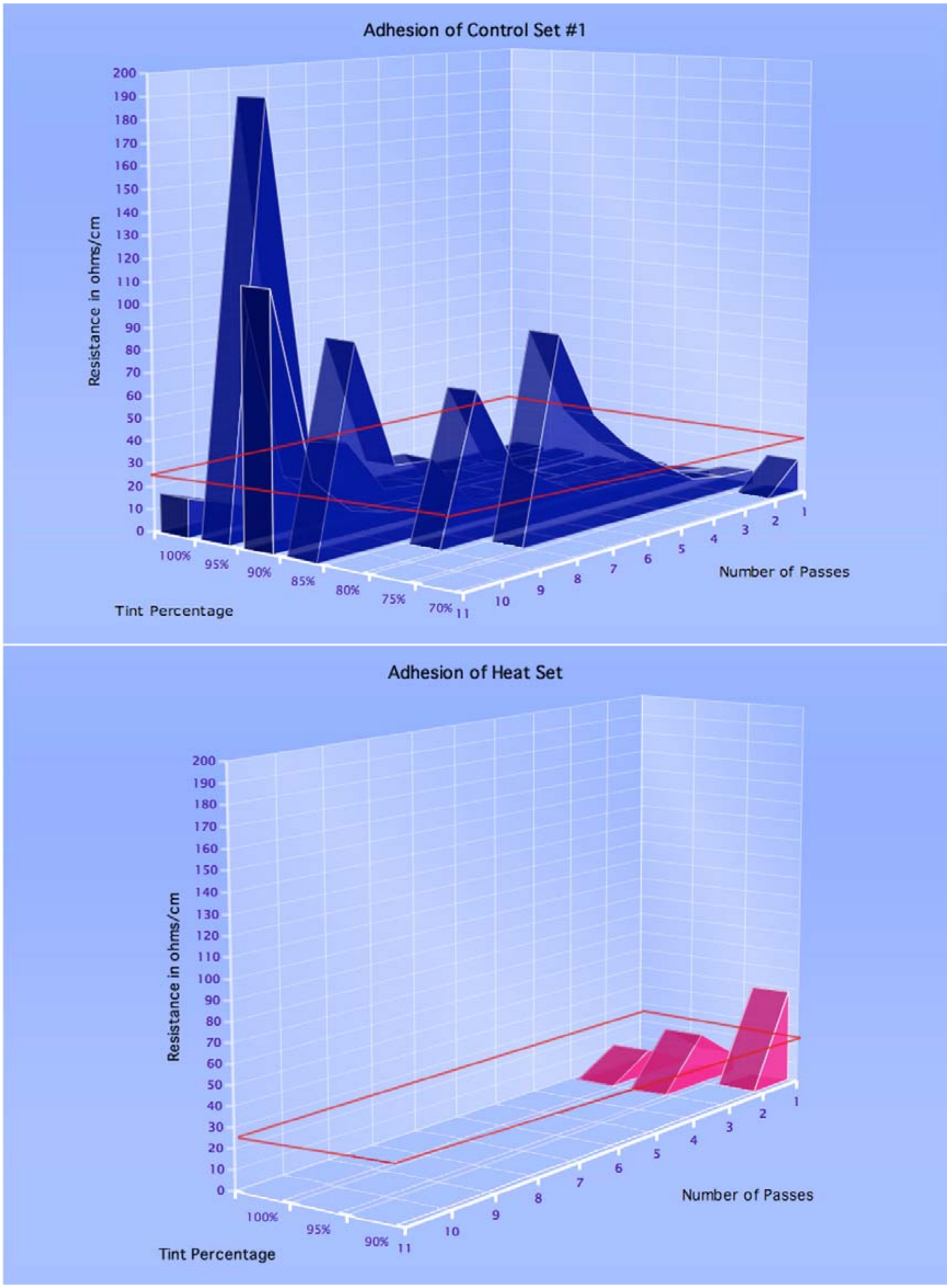

Figure 35: Adhesion Comparison of Control Set #1 vs. Heat Set

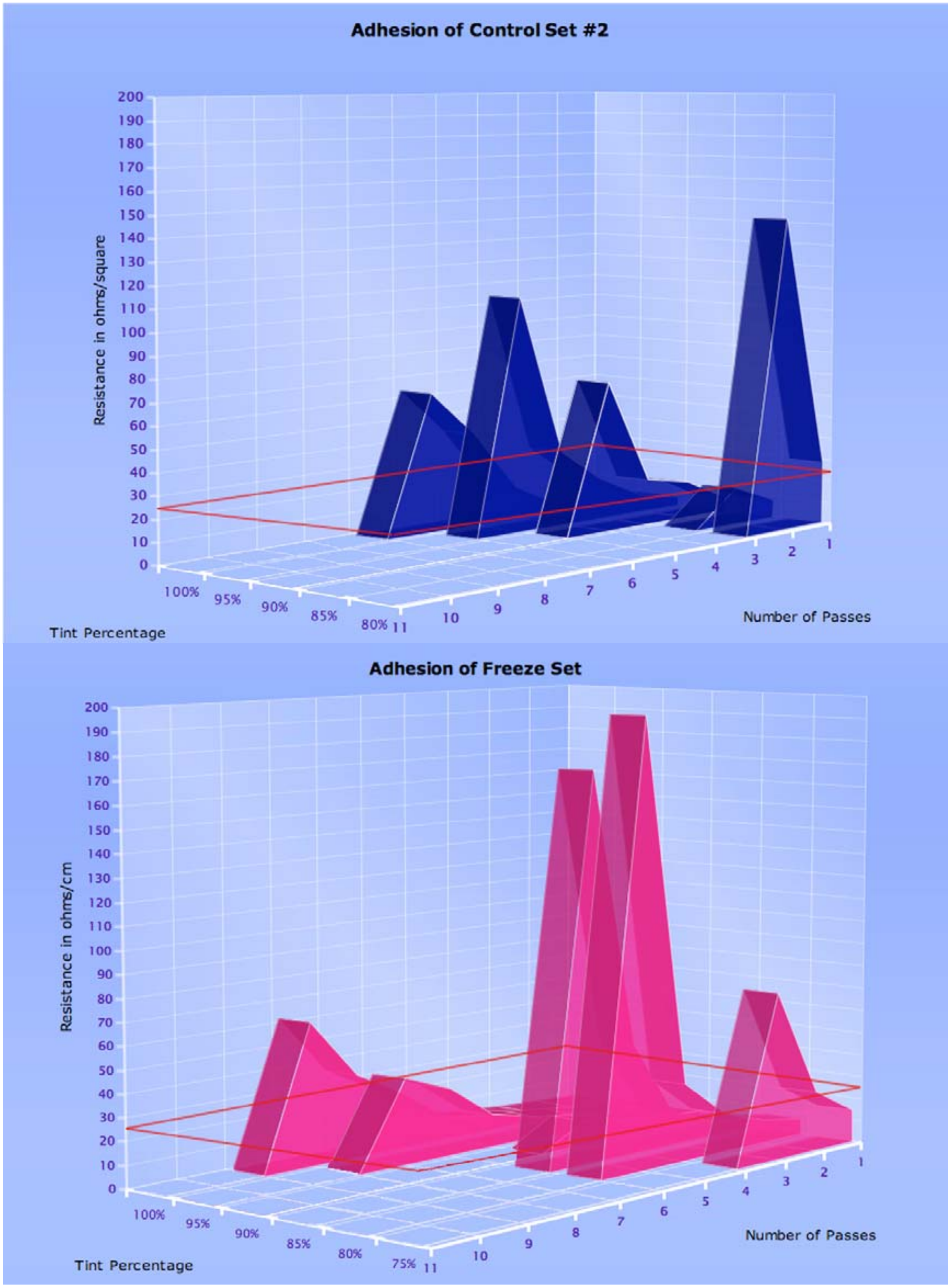

Figure 36: Adhesion Comparison of Control Set #2 vs. Freeze Set

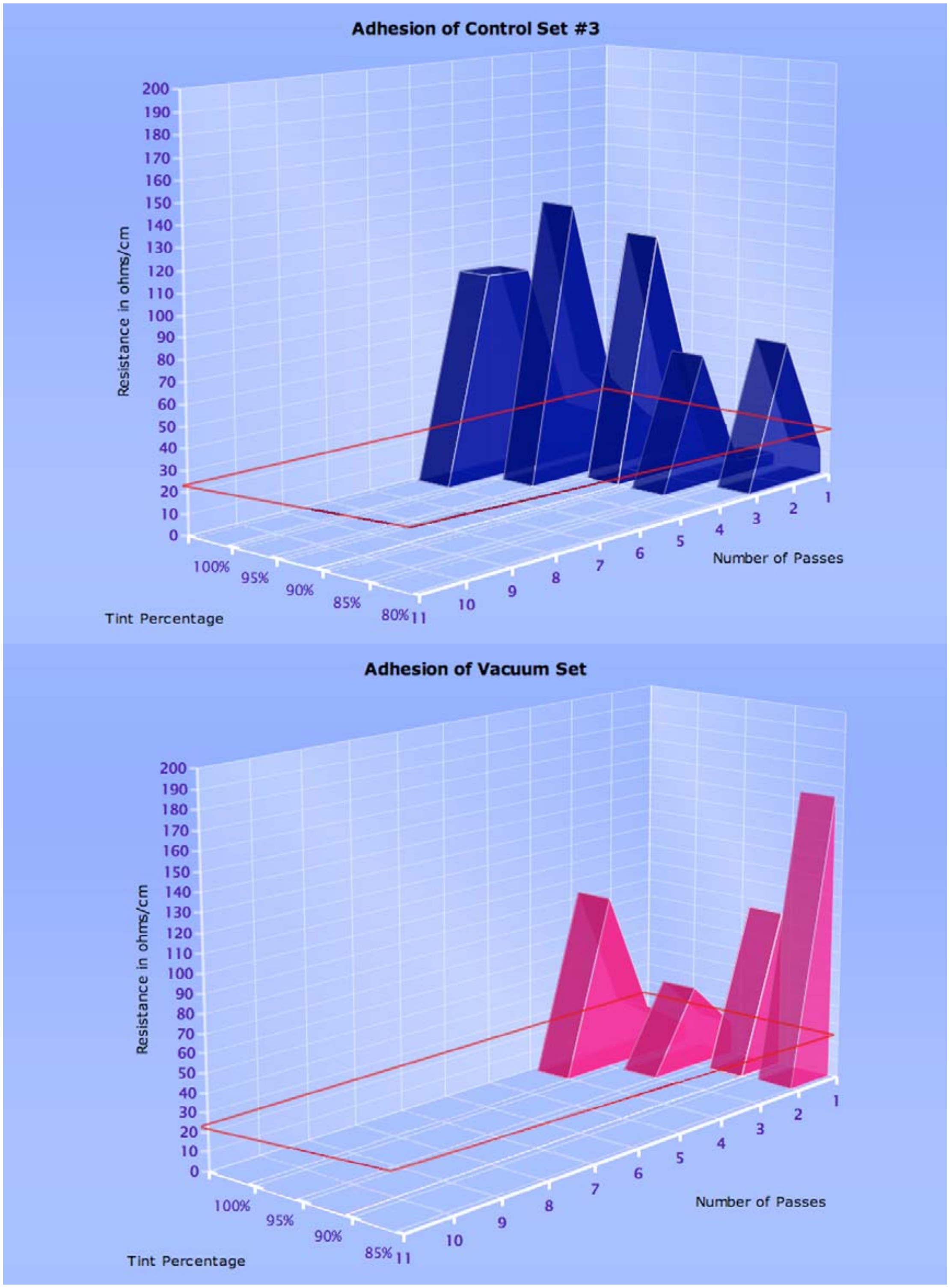

Figure 37: Adhesion Comparison of Control Set #3 vs. Vacuum Set

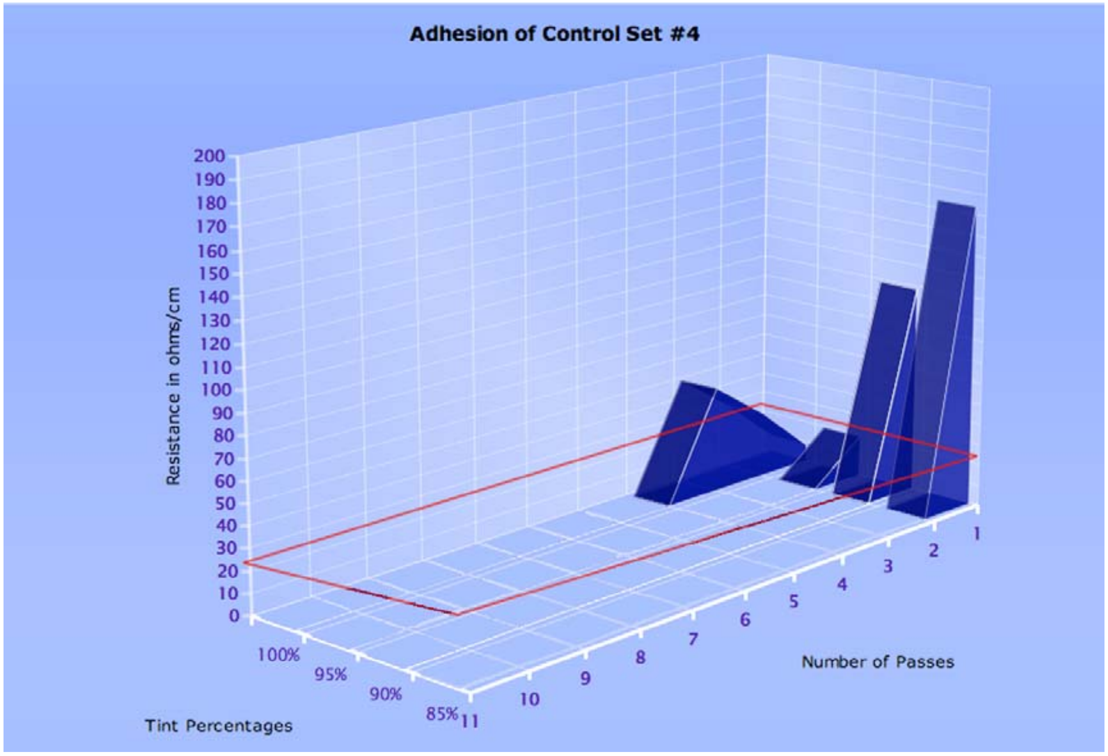

Figure 38: Adhesion Comparison of Control Set #4

Vacuum Condition. Figure 37 compares the adhesion of Control Set #3 and the Vacuum Set. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the acceptable level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. The conductivity of the Vacuum Set dropped off after the 85% tint patch while the Control Set dropped off after the 80% tint patch. Also, the number of passes it took to break the conductivity of the Vacuum Set was less than that of the Control Set. This shows that the vacuum condition had a negative effect on the adhesion properties of the print samples when compared to the Control Set.

Rain Condition. Figure 38 shows the adhesion of Control Set #4. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the acceptable level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. The Rain Set that is being compared to this Control Set is not graphed because the conductivity level broke on each tint patch after only one pass, resulting in infinite resistance for each measurement. The conductivity of the Control Set dropped off after the 85% tint patch, and the number of passes it took to break the conductivity of the Rain Set was significantly less than that of the Control Set. This shows that the rain condition had a severe negative effect on the adhesion properties of the print samples when compared to the Control Set.

Test D – Abrasion

The abrasion test was performed by attaching the print samples, print side up to a surface inclined at a 20^{o} angle. A piece of nylon substrate was attached to the bottom of a 500 g weight, and the weight was released at the top of the inclined block 10 times and a measurement of resistance was taken for each tint patch. This was repeated until the tint patch exhibited a measurement of infinite resistance, which indicated that the patch was no longer conductive. The number of passes it took to achieve this status for each patch of both the environmental set and control set sample was recorded and compared (Figures 39–42).

Discussion of Abrasion

Heat Condition. Figure 39 shows the abrasion of Control Set #1 and the Heat Set. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the acceptable level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. The conductivity level of the Control Set dropped off after 30 passes at a lower tint patch (75%) than that of the conductivity level of the Heat Set, which dropped off after 10 passes at the 80% tint patch. This indicates that there was little abrasive effect on the conductivity of the print samples of the Heat Set when compared to the Control Set.

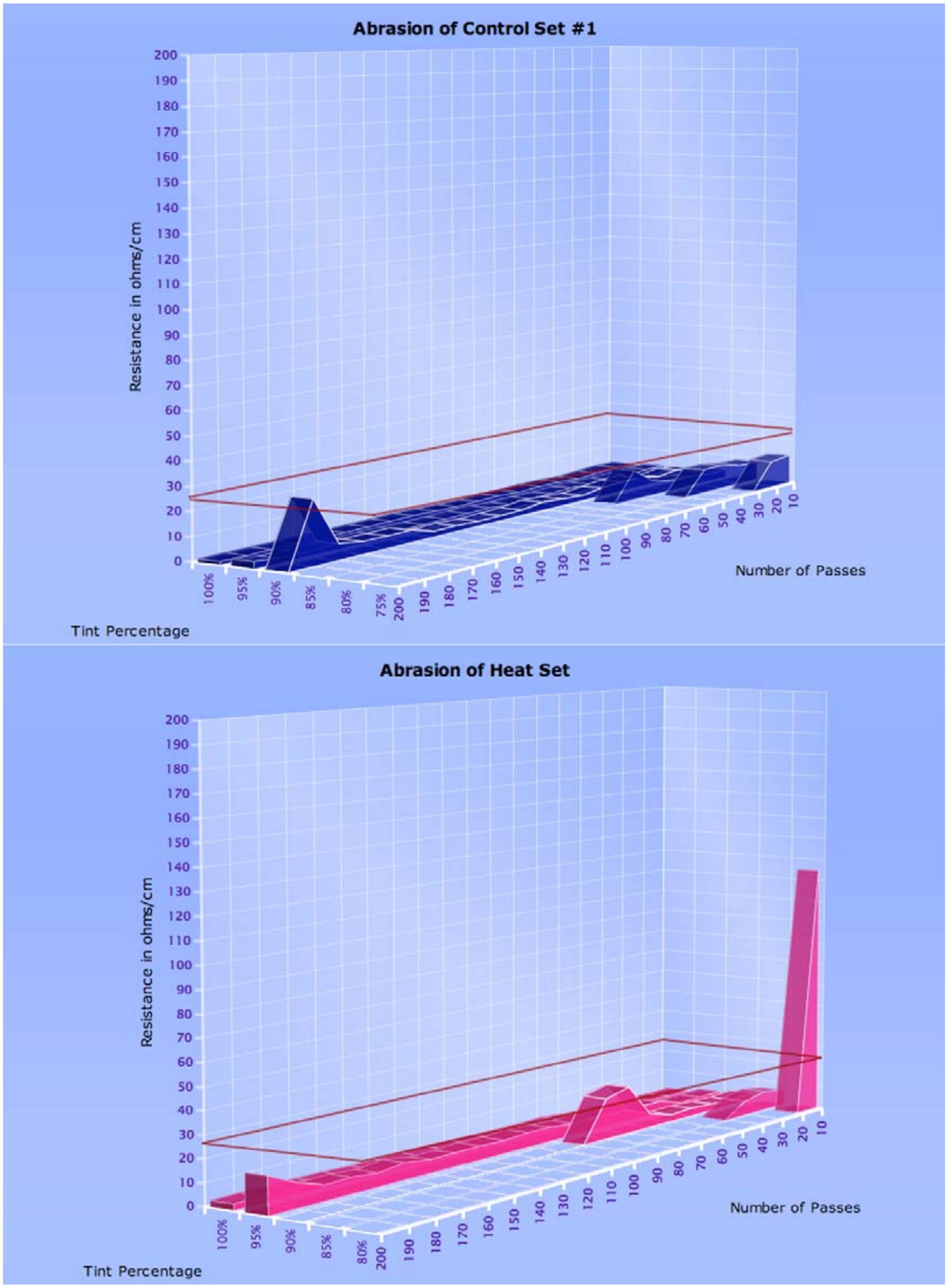

Figure 39: Abrasion Comparison of Control Set #1 vs. Heat Set

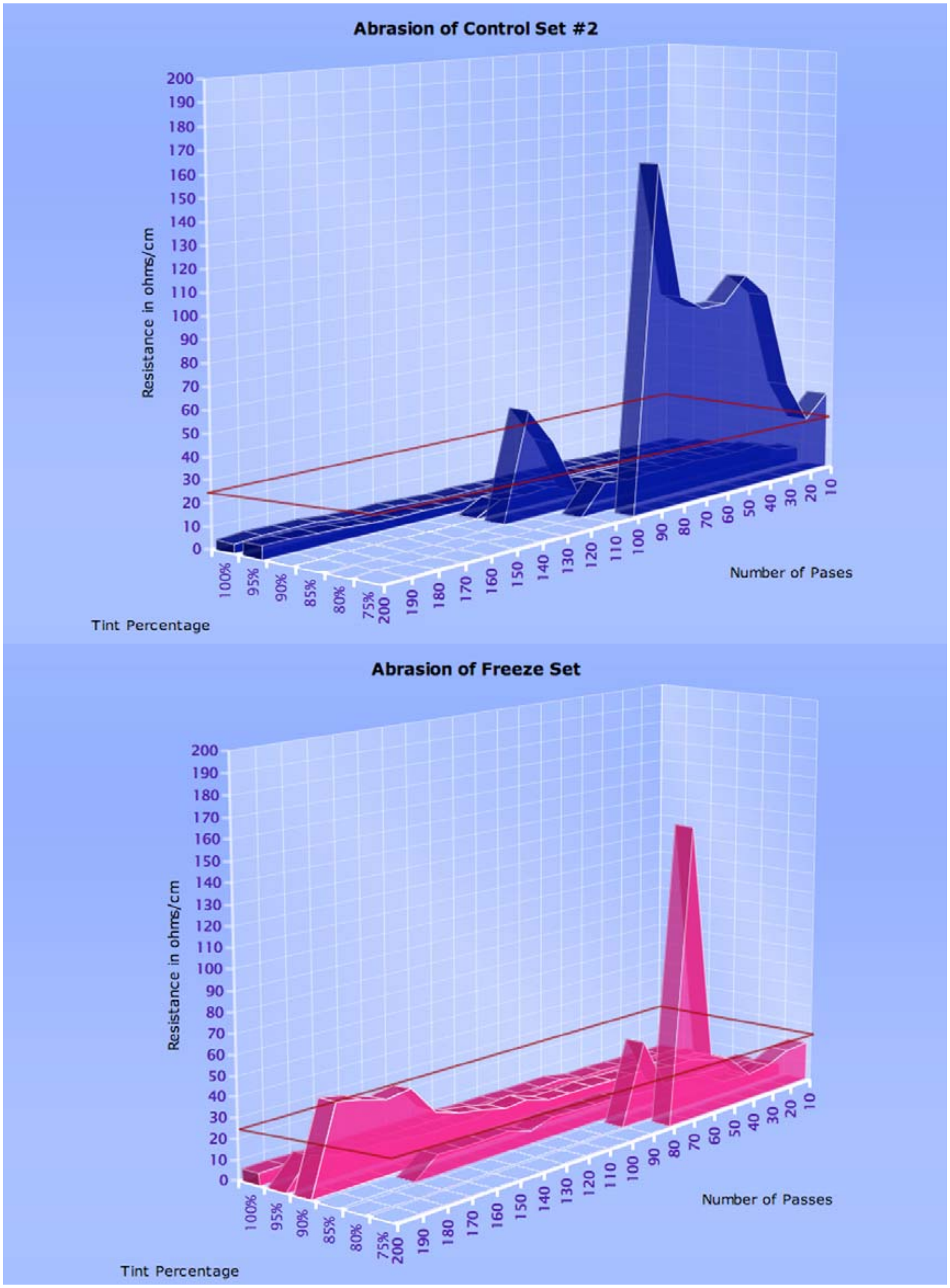

Figure 40: Abrasion Comparison of Control Set #2 vs. Freeze Set

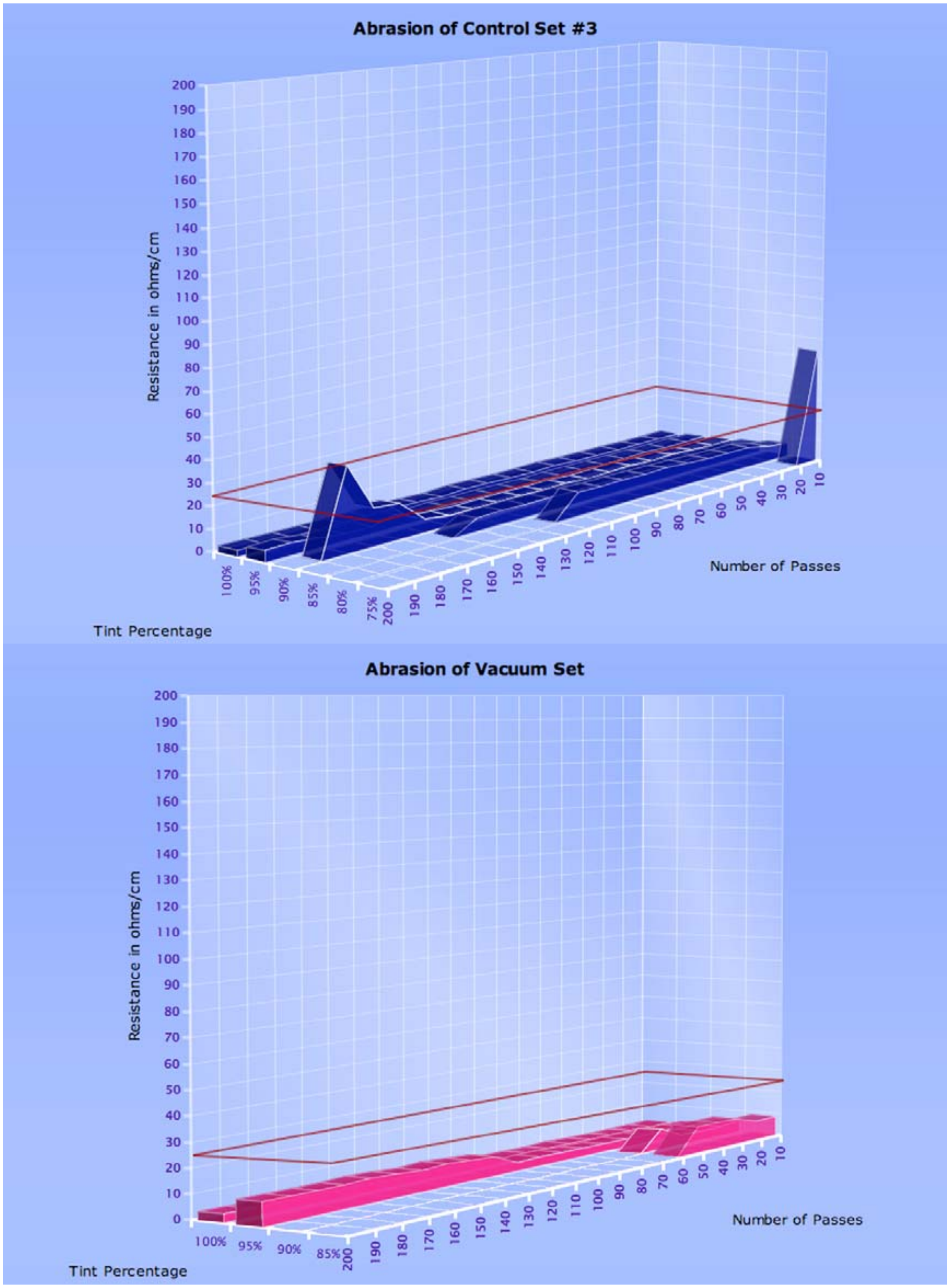

Figure 41: Abrasion Comparison of Control Set #3 vs. Vacuum Set

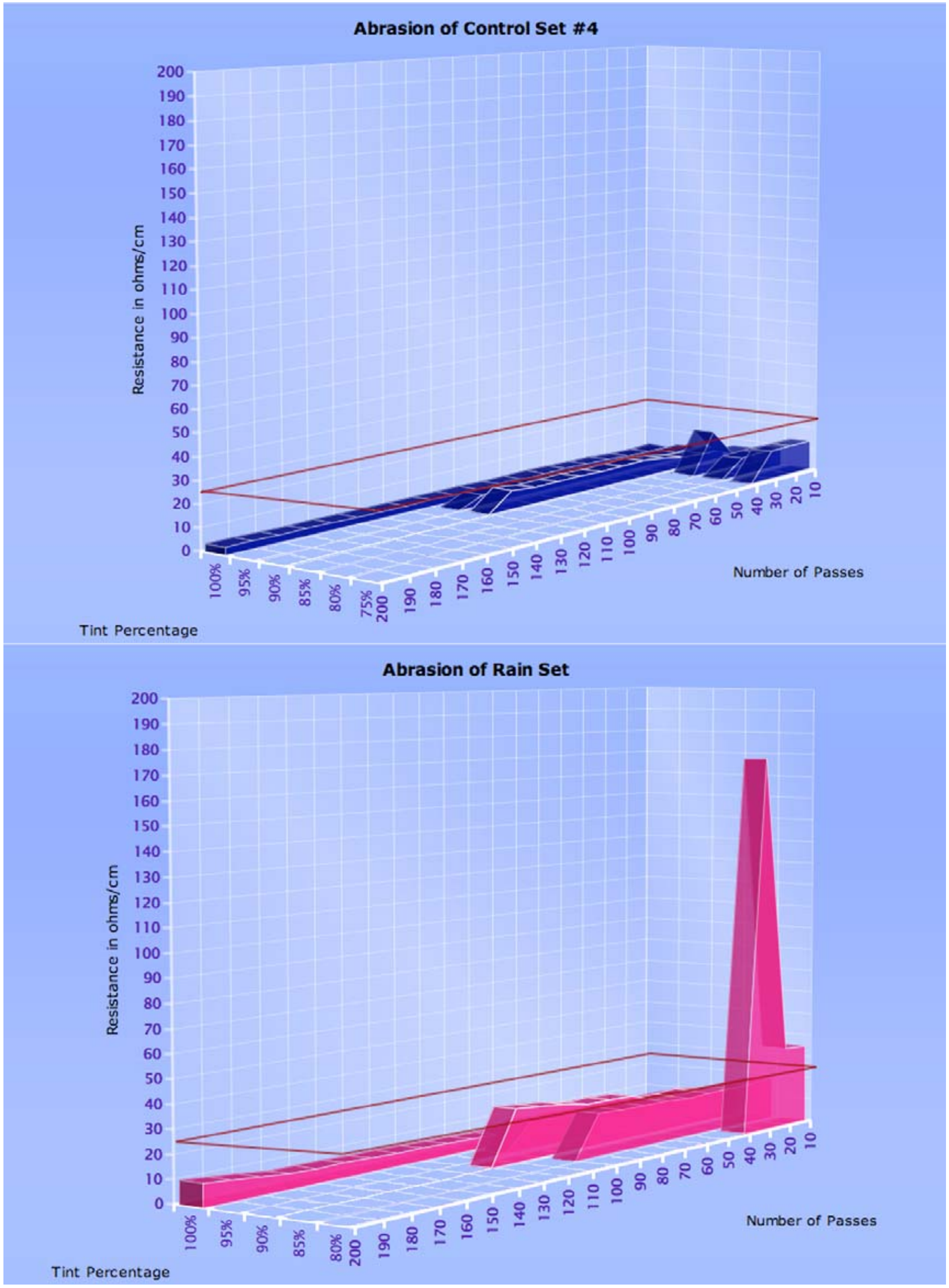

Figure 42: Abrasion Comparison of Control Set #4 vs. Rain Set

Freeze Condition. Figure 40 shows the abrasion of Control Set #2 and the Freeze Set. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the acceptable level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. The conductivity level of Control Set #2 dropped off after 100 passes at the 80% tint patch. The conductivity level of the Freeze Set dropped off after 80 passes at the 80% tint patch. This indicates that there was not a significant difference in resistance measurements between Control Set #2 and the Freeze Set. In this test, exposure to the freeze condition did not have an impact on the abrasion properties of the print samples.

Vacuum Condition. Figure 41 shows the abrasion of Control Set #3 and the Vacuum Set. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the acceptable level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. The conductivity level of Control Set #3 dropped off after 10 passes at the 75%

tint patch. The conductivity level of the Vacuum Set dropped off after 60 passes at the 85% tint patch. This indicates that there was a difference in resistance measurements between Control Set #3 and the Vacuum Set. In this test, exposure to the vacuum condition had an impact on the abrasion properties of the print samples.

Rain Condition. Figure 42 shows the abrasion of Control Set #4 and the Rain Set. The number of passes is indicated on the x-axis, the tint percentage value is indicated on the y-axis and the measurement of resistance in ohms/cm is indicated on the z-axis. The apex of the surface graph for each patch indicates the highest resistance measurement achieved. The decline of the graph that follows the peak is the number of passes where a failure of conductivity occurred resulting in a null measurement. The red box indicates the acceptable level of resistance permitted for use in production of an RFID antenna (25 ohms/square). Any measurement below this level passes for acceptable conductivity of the ink. The conductivity level of Control Set #4 dropped off after 40 passes at the 75% tint patch. The conductivity level of the Rain Set dropped off after 40 passes at the 80% tint patch. This indicates that there was a slight difference in resistance measurements between Control Set #4 and the Rain Set. In this test, exposure to the rain condition had an impact on the abrasion properties of the print samples.

Test E – Creasing

In each of the four control and environmental condition trials of this test, creasing each tint patch once caused an absolute resistance measurement. This indicates that any creasing of the print samples will cause infinite resistance. No determination can be made regarding the effect of any of environmental conditions on the creasing properties of the print samples. However, it can be determined that creasing any printed sample using the test ink and substrate will cause the conductivity of the print sample to break, thus rendering it ineffective.

Determination of Acceptable Ink Film Thickness

A caliper was used to measure an ink film thickness level that is acceptable for printed RFID antenna production. The thickness of the substrate was determined to be 0.2 mils. The thickness of each tint patch printed on the substrate was found and then the substrate thickness of 0.2 mils was subtracted to determine the ink film thickness (Table 5).

Table 5: Ink density level of print sample by tint percentage

Tint Percentage	**Ink Density Level**
100%	1.1 mils
95%	1 mils
90%	0.7 mils
85%	0.5 mils
80%	0.4 mils
75%	0.3 mils
70%	0.1 mils
60%	< 0.1 mils

A functional printed RFID antenna was measured to be 0.2 mils. This measurement was then established as the minimum acceptable ink film thickness for the purpose of this study.

Chapter 7

Summary and Conclusions

Environmental variables tested did not have an effect on the performance quality of silver RFID water-based flexographic ink when printed on a polyamide substrate for the 85–100% ink density levels. Environmental variables may have an effect on the performance quality of RFID water-based flexographic ink when printed on a polyamide substrate for the 70–80% ink density levels. The 100–75% tint patch ink density levels were deemed acceptable for use in production of RFID antennas because they meet the acceptable solid ink density level of 0.2 mils or greater for RFID antenna production. Although some effects of environmental exposure were observed for the 75% tint and below, these ink film thickness are unlikely to be printed.

Heat Set

Effects of the heat condition were apparent in the 70–80% tint patches for all ink tests except for the abrasion and crease tests. For the conductivity test, the heat condition effected the print sample by causing a rise in resistance levels of the ink.

Effects of the heat condition can also be seen in a change in density with increasing temperature. This is likely because heat application caused more complete ink film curing. Increased curing may result in a reduction of the amount of polymers present in the ink retaining matrix. This reduction will allow the silver particles to come more into contact.

It was anticipated that heat curing would have a positive effect on adhesion and abrasion resistance. Adhesion, however, was negatively impacted. Poor adhesion may have been the result of dimensional changes in the nylon with the application of heat. These dimensional changes would weaken the interfacial bond between the ink and substrate. There was not a significant impact on abrasion resistance of the sample.

The heat condition also caused a shift in color of the print sample. The heat set print sample produced L* values that were darker than that of the Control Set and the a*, b* values of the heat sample shift to more red values on the a* axis and more blue values on b* axis. The Delta E measurements calculated for all of the tint patches range from 5.67 to 9.33. The acceptable Delta E value in press environments ranges from 4 to 8. Therefore, the range that the Heat Set sample produced was still relatively within the acceptable range.

Freeze and Vacuum Set

Exposure to the freeze and vacuum conditions did not have a significant enough impact to indicate an effect on the print performance.

Rain Set

The rain condition exhibited some effect on the adhesion and abrasion properties of the print samples. Conductivity was lost after only one pass. After exposure to water the ink film was completely removed by the tape. The condition was also the only environmental variable to exhibit an impact on the abrasion resistance of the samples.

All effects on performance of the sample are likely due to the fact that this substrate is particularly hydrophilic and probably absorbed a significant amount of moisture from exposure to this condition. This absorption of water caused poor bonding between ink and substrate. It was determined that in a production environment some sort of coating or lamination would perhaps improve this problem. This could, however, have a negative effect on the conductivity of the sample.

Control Sets

The ink test results from comparing Control Sets #1–4 with the exception of color and abrasion indicated the ink itself has a negative effect on the performance of the print sample. The ink was very abrasive to the proofing press. It caused the cells of the anilox plate to plug up quickly even when cleaning was performed after each print sample was created. The ink corroded the plate and damaged the stereo roller of the press.

Lastly, the ink had shear thickening properties that caused many of the print samples to have a marred image that was not acceptable for use in testing procedures. Metallic particles in the ink are large and became concentrated at the point of the printing process where the doctor blade meters the ink onto the impression roller, thus causing a marred image. To correct this problem, careful observation of printing conditions was required and adjustments of the speed of the press were implemented.

Creasing Test

It was determined that creasing any antenna printed using this ink and substrate would render the antenna ineffective. Therefore, it appears that creasing has a negative impact regardless of exposure to environmental variables.

Summary

The 85–100% solid ink density levels of silver RFID water-based flexographic ink when printed on a polyamide substrate are not effected by exposure to environmental conditions of this study and therefore are acceptable for use in production of printed RFID antennas. This is important, because the ink density level is likely to be printed at 100%. This study would then show that use of this ink with a polyamide substrate similar to nylon 6,6 would be acceptable for print production.

Agenda for Further Research

Due to the scope of this project, sample size was limited to 40 prints with each ink testing procedure only conducted once. It is possible that a change in results would be seen by performing the same type of experiment with a larger sample size over an extended period of time. For the scope of this study, a flexographic proofer was used to create the print samples. An interesting way to increase the sample size for an experiment like this would be to use a commercial flexographic press capable of producing more prints that would allow for the use of a printing plate that is imaged with a functional antenna design. The results of a study conducted in this manner would more appropriately reflect the behavior of the ink and the substrate in a real-world application.

Also, to simulate a more realistic environment, the parameters of this study could be extended to test a fully formed package design that has completed the finishing and filling processes required before the product enters the packaging distribution system.

Another way to build off of this idea is to test the packaging after it has been exposed to the different environmental conditions over a longer time frame. This study only examined the performance of the ink over a 24-hour time frame. It is likely that the results would show more variability in ink performance if exposed to an environmental condition for perhaps a week or even over a year.

Finally, a way to extend the implications of the study to include a broader range of audience would be to include not only standard ink testing procedures but also standard package performance testing.

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